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# SOIL SCIENCE

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# SOIL SCIENCE



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## THE USE OF THE QUINHYDRONE ELECTRODE FOR MEASURING THE HYDROGEN-ION CONCENTRATION OF SOILS

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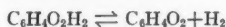
### HISTORICAL AND THEORETICAL

The electrometric method for determining the hydrogen-ion concentration of soils by means of the ordinary hydrogen electrode has never been entirely satisfactory. This is due to the fact that a constant voltage cannot be quickly and easily obtained. Often hydrogen has to be passed through the soil suspension for a long period of time before constant readings can be secured. In many cases accurate results cannot be obtained. In measuring the hydrogen-ion concentration of neutral or slightly alkaline soils, the carbon dioxide equilibrium enters into the reaction and the observed voltages are often misleading. The electrodes become abraded easily in sandy soils and only a few determinations can be made without replatinizing. Coupled with the difficulty of obtaining a constant potential, the care of the electrodes makes the method not only complicated and tedious but also very slow.

The colorimetric method has a limited application. It is satisfactory with clear soil extracts, but precise readings cannot be made with turbid suspensions. The method requires the use of a series of indicators and buffer mixtures which are likely to change with time and give inaccurate results.

In 1920, Biilmann (1, 3) showed that it was possible to form with the organic compound, quinhydrone, an electrode which could be used for making hydrogen-ion determinations and with which very constant voltages were possible. The quinhydrone molecule is apparently formed by the union of one molecule of quinone,  $C_6H_4O_2$ , and one of hydroquinone,  $C_6H_4O_2H_2$ . In an aqueous solution it is very highly dissociated into its components.

Hydroquinone and quinone, the products of the dissociation of the quinhydrone, are the active bodies of the electrode. According to the equilibrium equation,



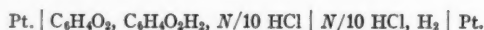
the concentration of hydrogen is represented by the formula:

$$(H_2) = \frac{(C_6H_4O_2H_2)}{(C_6H_4O_2)} \cdot K \quad (A)$$

<sup>1</sup> The writer expresses his appreciation for the helpful suggestions from Professors G. W. Conrey and R. M. Salter.

where  $K$  is a constant. The concentration of hydrogen at a given temperature, therefore, is "entirely determined by the proportion between the molecular concentration of the hydroquinone and the molecular concentration of the quinone, but which does not depend on the absolute concentrations of these bodies nor on the concentration of the hydrogen ions in solution."

Biilmann used an element composed of two electrodes: one, a platinum foil dipped into a solution of quinhydrone in decinormal hydrochloric acid and the other, the usual hydrogen electrode immersed in the same acid. This element is represented as:



The quinhydrone electrode is positive in respect to the hydrogen electrode.

At 18°C. he obtained a potential of 0.7044 volt using dry hydrogen under a pressure of one atmosphere. To transfer the voltage into conditions where humid hydrogen is used, 0.0002 volt must be subtracted from this value. The Sorensen formula for pH at 18°C. for a decinormal calomel electrode is

$$\text{pH} = \frac{E - 0.3377}{0.0577} \quad (\text{B})$$

in which  $E$  represents the observed voltage. By substituting  $0.7042 - E_q$  for  $E$  in equation B, the formula for pH at 18°C. for the quinhydrone electrode is derived

$$\text{pH} = \frac{0.3665 - E_q}{0.0577} \quad (\text{C})$$

$E_q$  is the observed voltage for the quinhydrone electrode.

In 1923, Biilmann (2) showed that this electrode was applicable in determining the hydrogen-ion concentration of soils. When it was compared with the ordinary hydrogen electrode good checks were secured. Up to the present time no standardization of methods for using this electrode has been published. It is the purpose of this paper to report certain studies which have been made of the factors which enter into the use of the quinhydrone electrode for measuring the reaction of soils. Consideration was given to the use of the saturated, normal, and decinormal calomel cells; to variation in the amount of quinhydrone; to measuring the constancy of potential; to comparing the quinhydrone and hydrogen electrodes; and to the effect of the soil-water ratio upon results secured with the quinhydrone electrode.

#### PROCEDURE

A test tube with a diameter of 2 cc. and a depth of 14 cc. was employed for holding the soil suspension and the quinhydrone. Into this was placed a platinum electrode, which was made by fusing a platinum foil 12 mm. square onto a stiff platinum wire that had been previously fused in the end of a Pyrex

glass tube. This composed the quinhydrone electrode. It was connected to the calomel cell by a saturated KCl agar bridge. The agar bridge was renewed whenever it exhibited signs of deterioration, which was indicated by cracks in the agar and by erratic voltages. Since the completion of this work, Schollenberger (6) has constructed a cell which eliminates the agar bridge. The care of the platinum electrode is a very important factor in this method. At the beginning of each day's work, the electrode was cleaned in a hot chromic acid solution, washed thoroughly with freshly boiled distilled water, and heated to redness in an alcohol flame. An ordinary gas flame cannot be used. After readings were made, the test tube containing the soil suspension-quinhydrone mixture was removed and the platinum electrode and agar bridge were thoroughly rinsed with distilled water. The cell was immersed in water of a known temperature while the readings were made and the appropriate temperature correction applied in each case. A Leeds and Northrup Type K Potentiometer and Type R galvanometer were used to measure the observed voltages.

#### EXPERIMENTAL

##### *The use of saturated, normal, and decinormal calomel cells*

Biilmann experimented with a decinormal electrode, with which the observed voltage is 0.7042. From this the formula for the hydrogen-ion concentration is derived as expressed in equation C. This is a direct substitution of his results in the equation derived from the Nernst formula,

$$E = E_0 - \frac{RT}{nF} \times 2.303 \log C \quad (D)$$

in which  $E$  = electrode potential corresponding to ionic concentration  $C$ ,

$E_0$  = electrolytic potential (electrode potential at molar concentration),

$R$  = the gas constant (8.32 joules per degree),

$T$  = absolute temperature ( $273^\circ + \text{temperature } C$ ),

$n$  = Valency of the ion,

$F$  = the faraday (96,500 coulombs)

$C$  = ionic concentration of the solution.

The value of  $\frac{RT}{nF} \times 2.303$  at  $18^\circ$  and  $25^\circ C$ . is 0.0577 and 0.0591, respectively.

From these values, using Biilmann's method of obtaining equation C and and the voltage 0.6988 as measured for the decinormal electrode at  $25^\circ C$ ., the formula for the hydrogen-ion concentration as expressed in pH can be derived.

$$\begin{aligned} E &= E_0 - 0.0591 \text{ pH} \\ 0.6988 - E_q &= 0.336 - 0.0591 \text{ pH} \\ \text{pH} &= \frac{0.3628 - E_q}{0.0591} \end{aligned} \quad (E)$$

In addition to the decinormal electrode both the normal and the saturated were used. For the normal electrode, using the same method of calculation as in equation E and the value 0.283 for  $E_0$ , the following equation is obtained:

$$\text{pH} = \frac{0.4158 - E_q}{0.0591} \quad (\text{F})$$

For the saturated electrode,  $E_0$  is 0.245 and the resulting equation is

$$\text{pH} = \frac{0.4538 - E_q}{0.0591} \quad (\text{G})$$

The temperature factor as determined in Biilmann's investigations is 0.77 millivolt per degree deviation from 25°C. Below this temperature the correction must be subtracted from  $E_q$ ; above 25° it must be added. A comparison of results secured with the three electrodes is shown in table 1.

These results indicate that any one of the three calomel cells may be used. The saturated electrode, however, is preferred for convenience. In the first

TABLE 1  
*A comparison of pH values for the saturated, normal and decinormal calomel cells*

NUMBER	SOIL TYPE	CALOMEL ELECTRODE		
		Saturated	Normal	Decinormal
30	Trumbull silt loam	4.63	4.65	4.67
6	Paulding clay	6.38	6.36	6.33
130	Dunkirk fine sand	5.22	5.22	5.20

place, it is more constant. The normalities of the normal and decinormal cells change more quickly than the saturated. Secondly, in soils that are neutral or slightly alkaline a negative potential is obtained at a lower pH with the normal and decinormal. For the saturated electrode, a negative voltage is produced at pH 7.68; for the normal, at 7.02; and for the decinormal, at 6.14. When a negative potential is obtained, the poles must be reversed. The saturated cell does not often require this reversal since most soils have a hydrogen-ion concentration lower than pH 7.68.

*The effect of varying the amounts of quinhydrone*

The weight of quinhydrone necessary to give a constant voltage in Biilmann's experiments was 0.1 gm. for every 15 cc. of solution. However, the results in table 2 indicate that 0.05 gm. suffices for accurate results. In acid soils 0.02 gm. is sufficient. Quinhydrone added in excess of 0.05 gm. did not produce further change.

A convenient method of adding the quinhydrone to the soil suspension is by using a small glass spoon, blown on the end of a glass tube. The spoon

holds about 0.05 gm. If a large number of determinations are to be made at one time, the process of measuring the quinhydrone for each determination can be eliminated by making a fresh 0.3 per cent solution of quinhydrone with boiled distilled water and by adding the resulting solution to the soil. This solution must be kept in a dark bottle because light tends to dissociate the quinhydrone. The solution cannot be used on the second day because of this dissociation. The results in table 3 show the relation between the addition of quinhydrone in solution and in the dry state directly to the soil suspension.

TABLE 2  
*Effect of varying the amounts of quinhydrone upon the observed pH of the soil suspension*

NUMBER	SOIL TYPE	AMOUNTS OF QUINHYDRONE PER 15 CC. OF H <sub>2</sub> O ADDED TO 15 GM. OF SOIL				
		0.01 gm.	0.02 gm.	0.03 gm.	0.04 gm.	0.05 gm.
		pH	pH	pH	pH	pH
41	Tyler silt loam	4.10	4.18	4.19	4.18	4.19
507	Cory silt loam	4.54	4.81	4.85	4.84	4.86
22	Wooster silt loam	6.81	7.04	7.11	7.22	7.22

TABLE 3  
*The pH values from two methods of adding quinhydrone*

NUMBER	SOIL TYPE	METHOD OF ADDING QUINHYDRONE	
		Directly to the soil suspension	In solution
22	Wooster silt loam	7.11	7.06
507 A	Cory silt loam	4.88	4.84
507 B	Cory silt loam	5.06	5.08
518	Cincinnati silt loam	5.55	5.50
41	Tyler silt loam	4.25	4.26

#### *Measuring the Constancy of Potential*

It is often difficult to obtain a constant voltage when using the ordinary hydrogen electrode. This difficulty is not so great with the quinhydrone method. With most soils the latter gives very constant readings and equilibrium is quickly reached. With alkaline soils, however, the voltage is not exactly constant and the readings must be taken immediately after adding the quinhydrone to the soil suspension. La Mer and Parsons (4), studying the application of the quinhydrone electrode to electrometric titrations, found that a constant voltage could not be reached in an alkaline solution with a pH above 8.0. They attributed this to the autoxidation of the hydroquinone. In measuring the hydrogen-ion concentration of soils, this factor is not of large significance because few soils with the exception of the alkali





soils have pH values as high as 8.0. Constant readings with soils below pH 8.0 are readily obtained (table 4).

During a 10-minute interval, the largest deviation of potential, with the exception of soil 523, corresponds to a difference in pH of 0.07. For most purposes this variation has no significance. In the alkaline soil the voltage varied almost 0.10 in pH during 3 minutes and for a 10-minute period reached a deviation of 0.33 in pH from the original reading. If the readings are made immediately, however, excellent checks between duplicate samples can be obtained. Several hundred samples studied with this electrode have given uniformly excellent results.

TABLE 5  
*Comparison of the quinhydrone and hydrogen electrodes*

NUMBER	SOIL TYPE	HYDROGEN ELECTRODE		QUINHYDRONE ELECTRODE	
		volts	pH	volts	pH
6	Paulding clay	0.6215	6.37	0.0800	6.37
30	Trumbull silt loam	0.5025	4.39	0.1788	4.66
41	Tyler silt loam	0.4825	4.02	0.2083	4.16
90	Newton very fine sandy loam	0.5815	5.69	0.1074	5.87
101	Fulton silty clay	0.6185	6.32	0.0720	6.46
130	Dunkirk fine sand	0.5415	5.01	0.1456	5.23
135	Newton loam	0.6035	6.06	0.0935	6.10
153	Clyde silty clay loam	0.5890	5.82	0.1136	5.76
321	Newton clay loam	0.5875	5.79	0.1035	5.93
501	Clermont silt loam	0.5355	4.91	0.1572	5.02
507	Cory silt loam	0.5340	4.89	0.1659	4.88
518	Cincinnati silt loam	0.5675	5.45	0.1240	5.60

*A comparison of the quinhydrone and hydrogen electrodes*

Biilmann (2) found a variation from 0 to 0.2 in the pH values secured between the quinhydrone and hydrogen electrodes in a series of 75 different soils. Most of the samples checked within 0.1 in pH. This is considered a good check, since a given soil often shows greater variation from time to time. Table 5 gives a comparison of the results secured by the use of the two electrodes in 12 different soils and shows a variation similar in magnitude to Biilmann's work. Only two soils deviate more than 0.2 in pH. The method previously outlined was used to determine the hydrogen-ion concentration of these soils. A soil-water ratio of 1:1 was used for the quinhydrone method and 1:5 for the ordinary hydrogen electrode method.

The ordinary hydrogen electrode gave erratic voltages with soils that were alkaline. The results indicate the reliability of the quinhydrone electrode for measuring the hydrogen-ion concentration of soils.

TABLE 6  
Effect of the soil-water ratio on the hydrogen-ion concentration of soils

NUM- BER	SOIL TYPE	HYDROGEN-ION CONCENTRATION						pH					
		Soil-water ratio						Soil-water ratio					
		2:1	1:1	2:3	1:2	2:5		2:1	1:1	2:3	1:2	2:5	
6	Paulding clay	$6.456 \times 10^{-7}$	$4.266 \times 10^{-7}$	$3.548 \times 10^{-7}$	$3.020 \times 10^{-7}$	$3.020 \times 10^{-7}$		$6.19 \times 10^{-7}$	$6.37 \times 10^{-7}$	$6.45 \times 10^{-7}$	$6.52 \times 10^{-7}$	$6.52 \times 10^{-7}$	
30	Trumbull silt loam	$2.754 \times 10^{-8}$	$2.188 \times 10^{-8}$	$2.089 \times 10^{-8}$	$1.995 \times 10^{-8}$	$1.863 \times 10^{-8}$		$4.56 \times 10^{-8}$	$4.66 \times 10^{-8}$	$4.68 \times 10^{-8}$	$4.70 \times 10^{-8}$	$4.73 \times 10^{-8}$	
90	Newton very fine sandy loam	$1.514 \times 10^{-8}$	$1.349 \times 10^{-8}$	$1.175 \times 10^{-8}$	$1.072 \times 10^{-8}$	$9.55 \times 10^{-9}$		$5.82 \times 10^{-8}$	$5.87 \times 10^{-8}$	$5.93 \times 10^{-8}$	$5.97 \times 10^{-8}$	$6.02 \times 10^{-8}$	
101	Fulton silty clay	$5.012 \times 10^{-7}$	$3.467 \times 10^{-7}$	$2.951 \times 10^{-7}$	$2.570 \times 10^{-7}$	$2.455 \times 10^{-7}$		$6.30 \times 10^{-7}$	$6.46 \times 10^{-7}$	$6.53 \times 10^{-7}$	$6.59 \times 10^{-7}$	$6.61 \times 10^{-7}$	
130	Dunkirk fine sand	$7.413 \times 10^{-6}$	$5.888 \times 10^{-6}$	$5.623 \times 10^{-6}$	$4.365 \times 10^{-6}$			$5.13 \times 10^{-6}$	$5.23 \times 10^{-6}$	$5.25 \times 10^{-6}$	$5.36 \times 10^{-6}$		
135	Newton loam	$1.072 \times 10^{-6}$	$7.943 \times 10^{-7}$	$6.761 \times 10^{-7}$	$6.026 \times 10^{-7}$	$5.623 \times 10^{-7}$		$5.97 \times 10^{-7}$	$6.10 \times 10^{-7}$	$6.17 \times 10^{-7}$	$6.22 \times 10^{-7}$	$6.25 \times 10^{-7}$	
153	Clyde silty clay loam	$2.291 \times 10^{-7}$	$1.738 \times 10^{-7}$	$1.413 \times 10^{-7}$	$1.318 \times 10^{-7}$	$1.148 \times 10^{-7}$		$5.64 \times 10^{-7}$	$5.76 \times 10^{-7}$	$5.85 \times 10^{-7}$	$5.88 \times 10^{-7}$	$5.94 \times 10^{-7}$	
321	Newton clay loam	$1.660 \times 10^{-8}$	$1.175 \times 10^{-8}$	$1.047 \times 10^{-8}$	$8.913 \times 10^{-9}$	$7.080 \times 10^{-9}$		$5.78 \times 10^{-8}$	$5.93 \times 10^{-8}$	$6.05 \times 10^{-8}$	$6.15 \times 10^{-8}$	$6.15 \times 10^{-8}$	
327	Newton fine sandy loam	$5.370 \times 10^{-8}$	$3.715 \times 10^{-8}$	$3.311 \times 10^{-8}$	$3.020 \times 10^{-8}$	$2.692 \times 10^{-8}$		$7.27 \times 10^{-8}$	$7.43 \times 10^{-8}$	$7.48 \times 10^{-8}$	$7.52 \times 10^{-8}$	$7.57 \times 10^{-8}$	
501	Clermont silt loam	$1.202 \times 10^{-8}$	$9.550 \times 10^{-9}$	$8.318 \times 10^{-9}$	$7.413 \times 10^{-9}$	$6.761 \times 10^{-9}$		$4.92 \times 10^{-8}$	$5.02 \times 10^{-8}$	$5.08 \times 10^{-8}$	$5.13 \times 10^{-8}$	$5.17 \times 10^{-8}$	
523	Genesee silt loam	$7.413 \times 10^{-9}$	$4.898 \times 10^{-9}$	$3.467 \times 10^{-9}$	$3.631 \times 10^{-9}$	$3.802 \times 10^{-9}$		$8.13 \times 10^{-9}$	$8.31 \times 10^{-9}$	$8.46 \times 10^{-9}$	$8.44 \times 10^{-9}$	$8.42 \times 10^{-9}$	
528	Crosby silt loam	$8.128 \times 10^{-7}$	$5.370 \times 10^{-7}$	$4.898 \times 10^{-7}$	$5.248 \times 10^{-7}$	$5.495 \times 10^{-7}$		$6.09 \times 10^{-7}$	$6.27 \times 10^{-7}$	$6.31 \times 10^{-7}$	$6.28 \times 10^{-7}$	$6.26 \times 10^{-7}$	

*Effect of the soil-water ratio on the hydrogen-ion concentration*

Salter and Morgan (5) having studied the effect of varying the soil-water ratio in determinations of hydrogen-ion concentration of soils by the ordinary hydrogen electrode method, came to the conclusion that a ratio of 1:5 might well be chosen as a standard ratio for such measurements. They pointed out that the variation of the hydrogen-ion concentration with varying

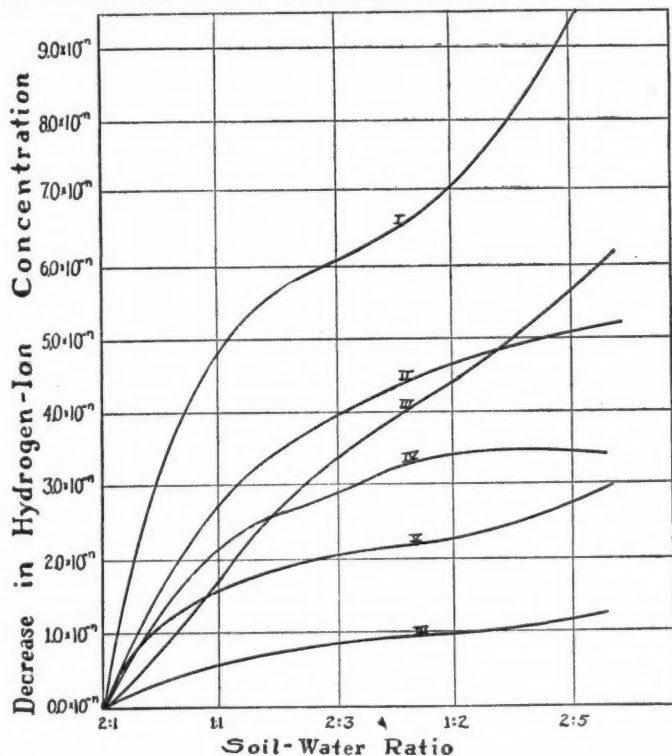


FIG. 1

- I = Soil 321.  $n = 7$ .  
 II = Soil 135.  $n = 7$ .  
 III = Soil 90.  $n = 7$ .  
 IV = Soil 6.  $n = 7$ .  
 V = Soil 327.  $n = 8$ .  
 VI = Soil 153.  $n = 6$ .

soil-water ratios could be described by a modification of Freundlich's adsorption isotherm. In the present study, variations in soil-water ratio were found to have an important influence upon the results secured with the quinhydrone electrode.

In this investigation 12 soils were studied with 5 different soil-water ratios, namely 2:1, 1:1, 2:3, 1:2, and 2:5. The soils vary from a fine sand to a heavy clay, and from a very acid soil to one distinctly alkaline. Table 6 shows the effect of varying the soil-water ratio on these soils.

It is apparent from the foregoing data that the hydrogen-ion concentration decreases as the soil-water ratio decreases. The same phenomenon has

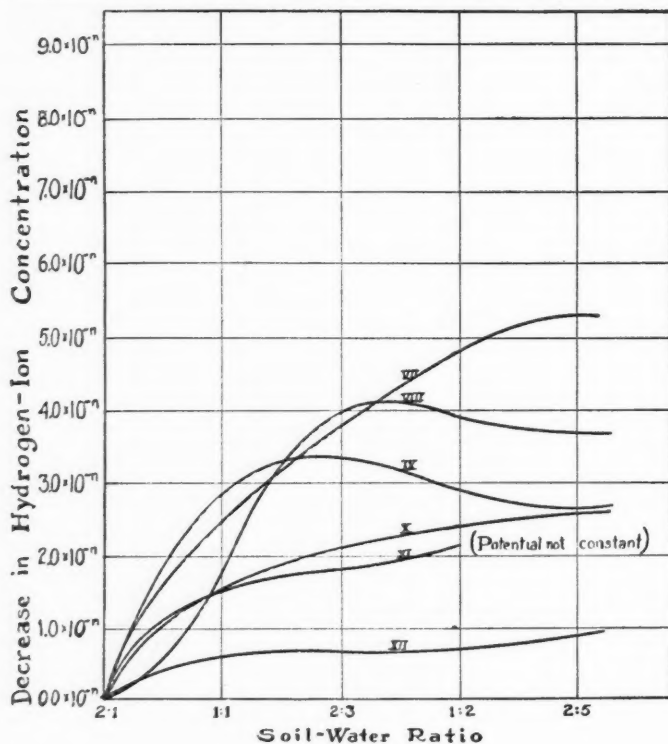


FIG. 2

- VII = Soil 501.  $n = 6$ .
- VIII = Soil 523.  $n = 9$ .
- IX = Soil 528.  $n = 7$ .
- X = Soil 101.  $n = 7$ .
- XI = Soil 130.  $n = 6$ .
- XII = Soil 30.  $n = 5$ .

been observed with the ordinary hydrogen electrode. In the results presented there is an almost consistent variation in pH of 0.3 between a ratio of 2:1 to 2:5. This shows the necessity of choosing some standard ratio to be used in this method. A comparison of these results with those in table 5



TABLE 7  
Conversion of voltage to pH with the quinhydrone electrode and saturated calomel cell

$E_q$	pH	$E_q$	pH
-0.0485	8.50	0.1052	5.90
-0.0455	8.45	0.1082	5.85
-0.0425	8.40	0.1111	5.80
-0.0396	8.35	0.1141	5.75
-0.0366	8.30	0.1170	5.70
-0.0337	8.25	0.1200	5.65
-0.0307	8.20	0.1229	5.60
-0.0278	8.15	0.1259	5.55
-0.0248	8.10	0.1288	5.50
-0.0218	8.05	0.1318	5.45
-0.0189	8.00	0.1347	5.40
-0.0160	7.95	0.1377	5.35
-0.0130	7.90	0.1407	5.30
-0.0100	7.85	0.1436	5.25
-0.0071	7.80	0.1466	5.20
-0.0041	7.75	0.1495	5.15
-0.0011	7.70	0.1525	5.10
+0.0018	7.65	0.1555	5.05
0.0047	7.60	0.1584	5.00
0.0077	7.55	0.1614	4.95
0.0107	7.50	0.1643	4.90
0.0137	7.45	0.1673	4.85
0.0167	7.40	0.1702	4.80
0.0197	7.35	0.1732	4.75
0.0226	7.30	0.1761	4.70
0.0256	7.25	0.1791	4.65
0.0284	7.20	0.1820	4.60
0.0313	7.15	0.1850	4.55
0.0343	7.10	0.1879	4.50
0.0372	7.05	0.1909	4.45
0.0402	7.00	0.1938	4.40
0.0431	6.95	0.1968	4.35
0.0461	6.90	0.1997	4.30
0.0491	6.85	0.2027	4.25
0.0520	6.80	0.2056	4.20
0.0550	6.75	0.2086	4.15
0.0580	6.70	0.2115	4.10
0.0609	6.65	0.2145	4.05
0.0639	6.60	0.2175	4.00
0.0669	6.55	0.2204	3.95
0.0698	6.50	0.2234	3.90
0.0728	6.45	0.2263	3.85
0.0758	6.40	0.2293	3.80
0.0787	6.35	0.2322	3.75
0.0817	6.30	0.2352	3.70
0.0846	6.25	0.2382	3.65
0.0875	6.20	0.2411	3.60
0.0905	6.15	0.2441	3.55
0.0934	6.10	0.2471	3.50
0.0963	6.05	0.2500	3.45
0.0993	6.00	0.2530	3.40
0.1023	5.95	0.2559	3.35
		0.2589	3.30

for the ordinary hydrogen electrode indicates that the ratio of 1:1 with the quinhydrone method and of 1:5 with the ordinary hydrogen electrode give practically similar values. The ratio of 1:1 seems to be best adapted for this work. A graphic representation of the data shows this more clearly.

In figures 1 and 2, the soil-water ratio is plotted against the decrease in hydrogen-ion concentration below that observed at a soil-water ratio of 2:1. This method gives a good graphic representation of the data. In most of the curves a decided break comes in the proximity of the ratio of 1:1. This is added evidence of the desirability of selecting the 1:1 ratio for measurements by the quinhydrone method.

#### *Conversion of volts into pH*

In order to facilitate the reading of the hydrogen-ion concentration in terms of pH, table 7 was computed from equation G. It may be used to eliminate calculations after each reading. It is adapted for use only with a saturated calomel cell.

Table 7 shows that for every pH 0.05 there is a corresponding difference of 30 millivolts. If the observed voltage lies between any of the above values, the pH can be estimated to the second place. The temperature factor is 0.77 millivolts per degree deviation from 25°C.

#### CONCLUSIONS

A study of the quinhydrone method for determining the hydrogen-ion concentration soils leads to the following conclusions:

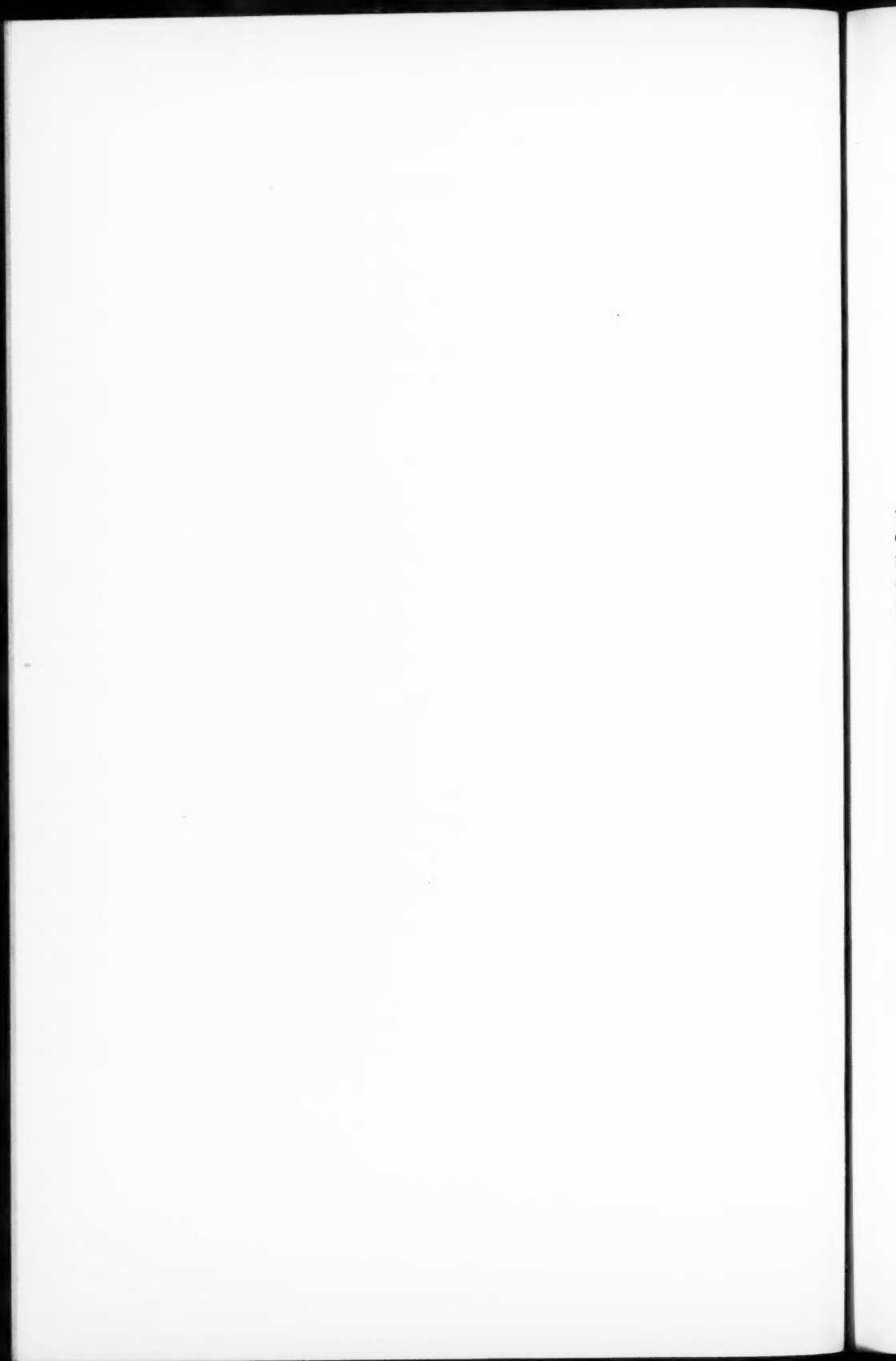
1. The saturated calomel cell is the most convenient to use since it is most constant and does not require a reversal of poles below pH 7.68.
2. For accurate results 0.05 gm. of quinhydrone per 15 cc. of solution is sufficient. The quinhydrone may be added in solution provided a fresh stock is prepared each day.
3. The potential is very constant with this electrode with the exception of soils above pH 8.0. It is reached quickly and easily.
4. The quinhydrone and ordinary hydrogen electrodes compare closely. Variations were obtained from 0 to 0.2 in pH, which is considered close enough for most soils work.
5. The most desirable soil-water ratio to use as a standard with the quinhydrone electrode is the ratio of 1:1. It gives results comparing closely with those obtained with the ordinary hydrogen electrode.

The quinhydrone method has a very distinct advantage over the ordinary hydrogen electrode inasmuch as the apparatus required is simpler, both in construction and operation, and requires a much shorter time to reach equilibrium. The method is applicable to field as well as laboratory purposes.

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## COLLOIDAL BEHAVIOR OF SOILS AND SOIL FERTILITY: II. THE SOIL COMPLEX CAPABLE OF BASE EXCHANGE AND SOIL ACIDITY<sup>1</sup>

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### INTRODUCTION

From the standpoint of soil genesis, dynamics, and methods of cultivation, those parts of the soil are of interest which show most activity in the soil processes and which create the differences among the various types. The native rock may be regarded as inert, for it adds no immediate fertility to the soil, although through the forces of weathering, the separation and formation of minute particles capable of taking part in the soil fertility processes occur. The larger particles play an important part mechanically. This mechanical support together with certain physical properties centered around the inert particles brings about a series of conditions which in their totality approximate what we know as soil fertility. The physical structure influences the aeration and thereby the oxidation processes which are chemical in nature.

If the practically inert quartz and other unweathered rock materials are excluded from the soil, the remaining portion will comprise the active components in which the life of the soil is centered. This portion of the soil has been named the zeolitic portion, but it is questionable whether the entire portion of the active soil is zeolitic. The vital importance of the organic portion in the life of the soil need not be emphasized here. None of the soil investigators would class these materials with the zeolites. This portion of the soil is very closely connected with what we understand under the term "colloidal fraction" of the soil. The process of soil development consists of the formation of this fraction and crystalloids, and the formation of various combinations and their distribution in the soil profile. The soil skeleton is passive and scarcely characterizes the types of soil. It is the so-called "colloidal fraction" which gives body and life to the soil, and which is in constant interaction with the soil solution, influencing its composition and suffering changes from the soil solution: it is this fraction which chiefly characterizes soils.

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<sup>2</sup> The authors share equal responsibility and credit for the work reported.



A further examination of this portion of the soil, shows that it is the one which is capable of base exchange, and it is this fraction, therefore, to which the soil investigator should direct his attention. A thorough appreciation of this soil complex capable of exchange will stimulate soil research in a definite direction. This trend of thought was clearly and extensively expressed by Sokolovski (13). The importance of such investigations has been pointed out also by Gedroiz (23) in his classical researches, by Hissink (7), by Wiegner (15), and by Kelley and Brown (11).

The extreme value of base exchange and of colloidal phenomena in investigations of soil problems has been demonstrated by the authors (8). In a footnote in one of the papers on "alkali soil studies" (8, paper III), the following statement was made:

The theory of base exchange as outlined for the zeolites through the replacement of their cations by the hydrogen ions of the sulfuric acid presents a new aspect of soil acidity. We may picture it as follows: A soil becomes acid when its so-called zeolitic portion (the portion capable of exchange) is saturated with hydrogen and there are no more basic substances to be replaced and come out in solution. Only then will free acids (mineral or organic) or acid salts appear in the soil solution. Until then no real acidity, i.e., free acid, is possible. The zeolitic portion saturated with hydrogen may show acidity when treated with neutral salts. In this case the replacement process described in this paper takes place; in other words, the cation of the neutral salt replaces the hydrogen. These considerations have been suggested in the course of the alkali soil investigations and are now being looked into.

In a recent publication Glinka (5), the noted authority on soil classification, points out that the process governing the formation of soils is to be the basis of soil classification. The parent rock has only a secondary influence upon the process. The conditions which determine the making up of the soil complex capable of exchange should be especially emphasized, as the study of base exchange is the logical step toward a rational and scientific understanding of soil processes.

It is to be remembered that all the work on base exchange is based on the researches of Way, Van Bemmelen and others. A critical analysis of the earlier work will be given in a later paper of this series. A comprehensive review may be found in the papers of Gedroiz (2) and a more concise review in the publication of the California Station (11).

#### PROBLEM OF SOIL ACIDITY

Investigations on several factors relating to base exchange and soil colloids have been instituted in the laboratories of the New Jersey Agricultural Experiment Station. The following is a report of studies made on a phase connected with the phenomena of base exchange; namely, soil acidity.

The question of acidity in soils resolves itself into that of the state of "saturation" or "unsaturation"—terms introduced by Gedroiz (3)—of the soil complex capable of base exchange. By "unsaturation" we understand a condition whereby the bases of the soil complex capable of exchange have

been replaced by hydrogen. "Saturation" is the reverse of unsaturation. A soil solution with a concentration of hydrogen ions in equilibrium with the bases capable of exchange will react acid upon extraction with water, on account of the free hydrogen ions present in it. If the concentration of the hydrogen ions in the soil solution in the state of equilibrium mentioned is not reinforced, the hydrogen ions may finally be adsorbed in the soil complex and replace bases such as sodium, potassium, calcium, and magnesium. A water extract of such a soil will not indicate any acidity, but in reality the soil is acid, since the soil complex is becoming unsaturated. Such acidity may be termed "potential" acidity. From these considerations we may readily see how all grades of acidity, or all stages of unsaturation may exist even though a water extract will not show it. To obtain an accurate measure of the acid present in soil, a quantitative estimation of the state of saturation or unsaturation, must be made. To get an insight into this question, a quantitative study of the hydrogen ions present in various soils has been undertaken.

While this work was in progress, a paper by Gedroiz (4) appeared giving his method, which varies but little from the one used at the New Jersey Station, based on Gedroiz's previous work. Gedroiz realizing that his quantitative measurements are open to criticism, because of the use of litmus and methyl orange as indicators, suggests the possibility of using electrometric titration.

Potentiometric measurements of such solutions with the hydrogen electrode are erroneous because of the  $\text{CO}_2$  factor. The bubbling of hydrogen through the solution to be tested forces out the  $\text{CO}_2$  and, since the solution is not buffered, no accurate reading can be obtained. It was found that the colorimetric method gave accurate readings when properly manipulated.

#### EXPERIMENTAL

Ten-gram samples of the soil were shaken with 250 cc. of normal  $\text{BaCl}_2$  solution, left in contact for 3 days, and filtered. The filtrate was then titrated with 0.02N KOH to pH 6.8. The soil on the filter paper was washed with  $\text{BaCl}_2$  solution, fresh portions of the solution being added after all the previous solution had drained off. This washing was continued until a sample showed a reaction similar to that of the pure  $\text{BaCl}_2$  solution. On the average it took from 3 to 5 liters of the normal  $\text{BaCl}_2$  solution. The solution was titrated with 0.02 N KOH to a pH 6.8, brom cresol purple and phenol red being used as indicators. At the same time water extracts of these soils were made in the usual manner and the pH values determined. The pH of the  $\text{BaCl}_2$  solution upon extraction was also determined.

The data in table 1 show that the water extracts of soils 6 and 7 with the pH of 6.4 and 6.2, respectively, give with the barium chloride solution a pH of 5.9 and 5.2, respectively. The water extract does not indicate any acidity, whereas the  $\text{BaCl}_2$  extract shows appreciable acidity. The other samples show the same tendency toward increasing the H-ion concentration with the

BaCl<sub>2</sub> solution extract. The explanation is simple. The Ba cations have a very high coefficient of adsorption and replacement and enter the portion of the soil capable of base exchange forcing out the hydrogen ions present there. The wide variations between the pH readings of the water extract and the BaCl<sub>2</sub> extract clearly indicate that the pH determination of water extract is valueless from the standpoint of determining acidity in soils. It gives only a measure of the free hydrogen ions present in the soil solution. On the other hand the pH readings of the BaCl<sub>2</sub> extract give an indication of the state of saturation of the soil. The titer indicates the total acid present in the soil, and the degree of saturation.

Much has been written on the subject of soil acidity and more is forthcoming; as a great number of excellent reviews on the subject are easily accessible there is no need of repetition. A recent publication by Hager

TABLE 1  
*H-ion concentration and titer of soil of Chenango series, Sussex Area*

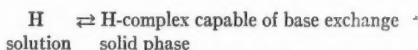
LABORATORY NUMBER	REACTION OF WATER EXTRACT	REACTION OF BaCl <sub>2</sub> EXTRACT	TOTAL TITRATABLE ACIDITY IN TERMS OF 0.02 N KOH
	pH	pH	cc.
1	5.4	4.6	10.05
2	5.4	4.6	15.00
3	5.4	4.6	11.55
4	5.2	4.8	8.60
5	5.2	4.8	8.85
6	6.2	5.9	1.90
7	6.0	5.2	3.85
8	6.0	5.8	2.10
9	5.6	5.2	3.70
10	5.8	5.4	4.05
11	5.0	5.0	5.75
12	5.8	5.8	1.30

(6), however, deserves attention. His work represents a reaction against the pH fad, which has flooded the literature on soil science. Hager bases all his arguments and investigations on the researches of Kappen (10), who maintains that there is no active acidity in mineral soils, at least in the great majority of the so-called acid soils. Under "active acidity"—a term introduced by Veitch (14)—Kappen understands titratable acidity of a water extract, which indicates the presence of free acid or acid salts.

Among the inorganic acids, sulfuric probably is the most generally found, since the sulfur compounds are biologically and chemically oxidized. The next acid of importance is nitric, which is an oxidation product of the nitrogen compounds. The other forms of free acid are the organic acids. In the process of decomposition of organic matter a number of organic acids of the methane, ethane, and other series appear. In the complicated system of the soil microbiological elements, there are times when organic acids are present

in the soil. They are, however, of transient nature, utilized by the various groups of microorganisms. Even the aforementioned inorganic acids are transient in nature, being affected by the bases released from the slowly decomposing silicates and compounds capable of base exchange. There is, however, a difference between the character of reactions in soil organic and inorganic acids. The organic acids in the process of decomposition leave as end-products  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which, in one way or another are taken care of in the soil. The inorganic acids, releasing their hydrogen chemically, are temporarily tied up in the soil complex capable of base exchange, but are ready to appear at any time, when other cations are introduced. The question of active acidity, or free acid, resolves itself into the following:

In making a study of the soil acids, on account of the dynamic nature of the organic and even inorganic acids, erratic results are to be expected, especially if a water extract is used either for pH or for titration determinations. For the determination of free acid, water must be used, since any other solvent introduces complications. From what has been said and from a knowledge of base exchange, one may readily appreciate the condition, when such free acids are possible. First come the less important (from the standpoint of distribution) soils of organic nature, like peat and muck. In these, free organic acids are to be expected. When we come to mineral soils the picture is somewhat obscure. There is possibly a condition whereby the hydrogen ions of the free acids are in equilibrium with the bases capable of exchange, e.g. the hydrogen ions are in preponderance in the soil solution and the complex capable of exchange is unsaturated. At this time the H ions are circling around, from true solution into the solid phase of the complex and back again into solution, replacing themselves and thereby only slightly affecting the other cations. It is for this reason that an acid soil after losing a certain amount of bases shows only slight amounts of bases in the drainage. The free acids from inorganic source may be represented diagrammatically.



The distribution of soils of an acid character as represented above is not so rare as was thought by Kappen (10), a view championed by Hager (6). *Undoubtedly soils that show a Sørensen value of pH 5.6 to 5.4 contain such free acids.* The free acid produced at this point may react with the silicates and bring aluminum and iron into solution. It is of interest to note that *precipitated  $\text{Al}(\text{OH})_3$  (the gel) will under certain conditions (anion effects) not go into the sol stage at pH 5.4 or even lower; the reaction is slow and in the presence of other electrolytes the conversion into gel may occur even at a low pH, e.g., the free acid may exist without aluminum in solution.* Experiments conducted in our laboratories corroborated the theory outlined.

A more detailed account of the work on Al and Fe in relation to pH and anions will be presented in a forthcoming paper.<sup>3</sup>

But leaving aside the active or free acid and approaching the subject of potential acidity, the replaceable H ions must be determined. For this purpose samples of soil from soil fertility plots 7A, 10A, 11A, and 12A of the New Jersey Experiment Station were used. Plot 7 receives no fertilizers; plots 10, 11 and 12 receive annual applications of 49.6 pounds of N per acre in the

<sup>3</sup> Since this paper has been written an interesting paper by Magistad (Soil Sci., v. 20, p. 181-227) on the Al problem has appeared. See also Niklas and Hock, 1925, Ztschr. Pflanzenernähr. u. Düngung., v. 5, p. 370-392.

forms of  $\text{Ca}(\text{NO}_3)_2$  of  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{CaCN}_2$ , respectively. All plots except 7, receive an annual application of 102.4 pounds of  $\text{P}_2\text{O}_5$  per acre in the form of acid phosphate and 160 pounds of  $\text{K}_2\text{O}$  in the form of  $\text{KCl}$ .<sup>4</sup>

Ten-gram samples were weighed out in Erlenmeyer flasks; 250 cc. of normal  $\text{BaCl}_2$  was poured over them and allowed to stand for various periods of time, with stirring at intervals; the solution was filtered, titrated with 0.02*N*  $\text{KOH}$ , and the amount of acid calculated for each period. After 10 days of contact solution and soil were transferred on a filter and washed with  $\text{BaCl}_2$  solution, as described, until the filtrate gave the same reaction in terms of pH as the  $\text{BaCl}_2$  solution. The filtrate was titrated and the total amount of acid cal-

TABLE 2  
*Hydrogen-ion concentration, titer, and speed of replacement of H-ions in soils variously treated*

LABORATORY NUMBER	KIND OF SOIL, PLOT NUMBER, AND YEAR OF SAMPLING	REACTION OF WATER EXTRACT	REACTION OF $\text{BaCl}_2$ EXTRACT	TITRATION OF 250 CC. $\text{BaCl}_2$ EXTRACT AFTER ONE HOUR*	TITRATION OF 250 CC. $\text{BaCl}_2$ EXTRACT AFTER 10 DAYS*	TOTAL TITRATABLE ACIDITY*	ACID EXTRACTED AFTER 1 HOUR CONTACT WITH $\text{BaCl}_2$	ACID EXTRACTED AFTER 10 DAYS CONTACT WITH $\text{BaCl}_2$
		pH	pH	cc.	cc.	cc.	per cent	per cent
	1914							
1	7A	5.6	4.8	2.20	4.15	9.60	23.0	43.2
2	10A	5.4	5.0	2.05	2.70	8.15	25.1	33.1
3	11A	5.4	4.4	4.40	6.70	14.40	30.5	46.5
4	12A	5.6	5.2	1.45	2.60	7.50	20.0	34.6
	1918							
5	7A	5.4	4.8	3.10	4.75	11.15	27.7	42.6
6	10A	5.6	5.0	1.70	2.95	8.15	20.8	36.2
7	11A	5.0	4.4	6.45	9.20	17.80	36.2	51.7
8	12A	5.6	5.1	1.05	2.20	6.80	16.0	32.3
	1922							
9	7A	5.2	4.6	4.10	6.50	12.15	33.7	53.5
10	10A	5.4	5.0	2.45	3.50	9.35	26.2	37.3
11	11A	4.8	4.4	7.75	12.10	22.30	34.7	54.2
12	12A	5.6	5.0	1.30	2.80	7.05	18.4	39.6

\* In terms of 0.02 *N*  $\text{KOH}$ .

culated. Wherever fairly large quantities of aluminum were apparent, allowances were made.

Table 2 gives the data of the experiment described. Again the pH figures of the water extract and those of the  $\text{BaCl}_2$  extract do not correspond. Invariably the  $\text{BaCl}_2$  extract shows more acidity than the water extract. This corroborates the statement made in connection with the Chenango soils (see table 1) that a determination of the H-ion concentration on a water extract does not give the true state of saturation and of unsaturation of the soils.

<sup>4</sup> For a detailed description of these plots the reader is referred to the annual reports of the New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology. The samples used were those taken from the plots in 1914, 1918, and 1922.



The data with  $\text{BaCl}_2$  extract show that the soils, even the check plot, were acid and unsaturated in 1914. These figures give us only a qualitative picture, as may easily be deduced from a comparison of the pH determinations of the plots for the different years. They are practically the same, and yet the titration figures show how these soils gradually but surely become unsaturated.

It should be remembered that the soils contain in their complex capable of exchange a large amount of hydrogen; that when the stage of hydrogen aluminum silicates is reached and other bases, like Na, K, and Mg, are replaced, the soil becomes extremely acid; and that the water extract of such a soil is turbid<sup>5</sup> containing free aluminum. Preliminary experiments conducted to bring about a completely unsaturated condition (by washing with 0.05*N* HCl until practically no test for Ca or Mg in the filtrate could be obtained) showed that these hydrogen aluminum silicates are colloidal in nature, forming a colloidal sol when treated with water. Such a condition is being approached by plot 11A with a pH (water extract) of 4.6 to 4.8; the extract is turbid, for it contains an appreciable amount of silica and aluminum also some unsaturated organic complexes capable of base exchange. Long before all the bases are replaced free acid appears and the more acid the soil becomes the slower the remainder of the bases is replaced, for reasons pointed out; namely, the hydrogen ions are replacing themselves attacking the other bases but slightly. In the long run, however, all the bases are being replaced by hydrogen.

The titration data afford a clear picture of the amount of acid present in the soil complex capable of exchange, e.g., in the silicates known as "zeolites" and in the acid humates. It has been shown by Gedroiz (4) and Sokolovski (13) that humus contains various cations capable of exchange inequivalent quantities. Unsaturated humus may contain no basic cations at all. The titration data, therefore, give us the sum total of free or active acidity and of potential acidity of soils.

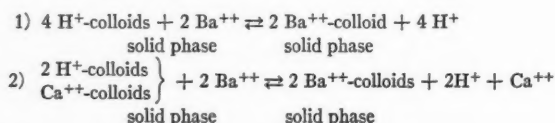
The figures in table 2 on the percentage of acid extracted after the first hour and after 10 days bring out some interesting features. First they show that after the first hour, as high as 36 per cent of the replaceable hydrogen was extracted from some soils. This indicates that the replaceable hydrogen is in a condition to be released from the solid phase (the complex capable of exchange) at certain equilibrium disturbances, notwithstanding the fact that in general the hydrogen ions stick very tenaciously in the solid phase.

Another feature to be noticed is the speed with which soils with various degrees of replaceable hydrogen give them up. The more acid soils suffered a loss of over 50 per cent of their replaceable hydrogen after 10 days of contact with the  $\text{BaCl}_2$  solution; the less acid soils gave up only 32 to 37 per cent. The explanation must be sought in the energy of adsorption and replacement,

<sup>5</sup> The turbidity of such acid solutions is partly due to the unsaturated condition of the fraction of humus capable of base exchange. This subject will be taken up at a later date.

or as we called it "coefficient" of adsorption and replacement of the various cations. A soil less unsaturated (10A or 12A) contains in the solid phase in equilibrium with the soil solution, beside the hydrogen ions, some Ca and other cations. Introducing the Ba ion with a coefficient of replacement higher than the Ca, forces the latter out more energetically than the hydrogen ions, which possess a coefficient of adsorption higher even than Ba. However, on account of the great excess of the Ba ions (normal solution) the reaction in virtue of the mass action brings out some hydrogen ions. On the other hand in soil 11A with the hydrogen ion predominating in the solid phase, the Ba ion must struggle chiefly with hydrogen ions. Thus a greater speed of replacement results.

In the form of chemical equations the various reactions may be represented as follows:



Thus in equation 1, representing the more acid soils, more H-ions are to be expected with the same number of Ba ions entering the complex.

These considerations open up the problem of the effects of fertilization on replacement of cations; this subject will be touched upon presently.

The process of continuous washing of the soil with the neutral  $\text{BaCl}_2$  solution to obtain all the replaceable hydrogen from the complex is slow. In order to speed up the reaction the use of the normal solution has been found to be the most practical, although higher concentrations of  $\text{BaCl}_2$  did replace the hydrogen somewhat faster. The cost involved did not warrant the use of concentrations higher than normal, and in many instances 0.5 *N* has given just as good result. Table 3 gives a few figures<sup>6</sup> on the effect of concentration of  $\text{BaCl}_2$  on replacement of hydrogen ions. It is apparent that the higher the concentration the faster is the replacement, but the increase in replacement is in no way proportional to the concentration.

There is, however, another phase of the subject which the data in table 3 suggest; namely, the effect of fertilization on the process of replacement.

One may easily surmise that even after a heavy application of fertilizers the soil solution will not at any moment contain a concentration of salts equivalent to normal. The tendency is toward a dilute solution and for this reason one should expect neither any rapid accumulation, nor any release of hydrogen ions. This subject is of extreme importance and as more data will accumulate in connection with the study of the capacity of the soils for base exchange, more light will be shed on this interesting phase of the work.

<sup>6</sup> More data on this phase of the subject are on hand, but being of the same nature as in table 3 they are omitted here.

TABLE 3

*Effect of concentration of replaceable cations on replacement of hydrogen ions*

KIND OF SOIL AND CONCENTRATION OF BaCl <sub>2</sub> SOLUTION	0.02 N KOH USED IN TITRATION OF BaCl <sub>2</sub> EXTRACTS* AFTER:						
	1 day	2 days	4 days	5 days	6 days	7 days	8 days
	cc.	cc.	cc.	cc.	cc.	cc.	cc.
<i>7A</i>							
0.001 N	0.30	0.37	0.20	0.25	0.30	0.40	0.25
0.01 N	0.65	0.37	0.50	0.40	0.40	0.40	0.50
0.1 N	1.50	1.00	1.40	1.30	1.15	1.20	1.25
0.5 N	1.65	1.90	1.95	2.05	2.10	2.05	2.20
<i>10A</i>							
0.001 N	0.40	0.20	0.25	0.18	0.30	0.25	0.30
0.01 N	0.45	0.30	0.35	0.35	0.35	0.25	0.35
0.1 N	0.80	....	0.60	0.65	0.70	0.70	0.70
0.5 N	1.05	....	1.10	1.10	1.15	1.30	1.20
<i>11A</i>							
0.001 N	0.65	0.35	0.45	0.35	0.45	0.40	0.40
0.01 N	1.75	1.20	1.50	1.45	1.40	1.30	1.40
0.1 N	2.90	3.10	3.35	3.10	3.20	2.90	3.05
0.5 N	3.85	3.90	4.30	4.20	4.25	4.20	4.35
<i>12A</i>							
0.001 N	0.30	0.15	0.25	0.15	0.25	0.20	0.25
0.01 N	0.45	0.10	0.35	0.30	0.30	0.20	0.20
0.1 N	0.50	0.20	0.30	0.30	0.45	....	0.30
0.5 N	0.40	0.75	1.00	0.95	0.90	0.60	0.75

\* 5 gm. of soil with 125 cc. of BaCl<sub>2</sub> solution was used.

TABLE 4

*Effect of temperature on speed of replacement of cations in soils*

SOIL NUMBER	BaCl <sub>2</sub> EXTRACTS*	
	1 hour at 65°C.	Room temperature
	cc. 0.02 N KOH	cc. 0.02 N KOH
181	3.50	3.60
182	8.15	8.50
187	3.35	3.40
188	2.30	2.85
191	2.25	2.40
192	0.45	0.60
189	0.80	0.95
190	0.45	0.50
197	0.80	1.10
198	0.90	0.95
193	1.95	1.95
194	0.45	0.60

\* 10 gm. of soil with 250 cc. of normal BaCl<sub>2</sub> were used.

It is known in general that heat speeds up chemical interaction. On an average, other things being equal, every rise of  $10^\circ$  doubles the amount of material changed each second.

In an attempt to speed up the reaction of replacement, by heating, several series of experiments were conducted. The soils were mixed with normal

TABLE 5  
*Titrateable acidity with normal  $\text{BaCl}_2$  and  $\text{KCl}$  solution extracts at various contact intervals*

SOIL NUMBER	$\text{BaCl}_2$ EXTRACT						$\text{KCl}$ EXTRACT				
	cc. of 0.02 N KOH after:						cc. of 0.02 N KOH after:				
	1 hour	1 day	3 days	5 days	7 days	10 days	1 day	3 days	5 days	7 days	10 days
<i>Plot soils</i>											
1914											
7A	2.20	2.90		3.50	4.00	4.15		2.55		2.65	
10A	2.05	2.60		2.90	2.90	2.70		1.80	1.90	1.85	
11A	4.40	5.25		6.05	6.70	6.70					
12A	1.45	2.00	2.20		2.50	2.60		1.60	1.50	1.60	
1918											
7A	3.10	4.10	4.20		4.60	4.75		3.20	3.50	3.20	3.55
10A	1.70	2.20	2.00		2.90	2.95		1.85	1.90	2.00	2.30
11A	6.45	7.90	8.50		9.60	9.20		8.25	8.10	8.60	8.60
12A	1.05	1.70	1.70		2.20	2.20		1.20	1.15	1.80	1.70
1922											
7A	4.10	5.35	5.60		6.30	6.50		4.80	5.00	5.10	5.25
10A	2.45	2.75	3.00		3.35	3.50		2.00	1.95	2.55	2.40
11A	7.75	9.65	10.55		11.60	12.10		10.50	10.80	10.80	11.20
12A	1.30	2.15	2.15		2.25	2.80		1.55	1.60	1.80	1.80
<i>Chenango series</i>											
SOIL SURVEY NUMBER											
181	3.60	4.60	4.80	4.80	5.25	5.05	2.60	2.50	2.80	2.90	3.05
182	8.50	9.40	9.40	9.50	9.95	9.80	9.60	10.20	10.80	10.65	10.75
187	3.40	4.65	4.95	5.10	5.35	5.40	4.90	5.30	5.35	5.75	5.65
188	2.85	3.10	3.35	3.25	3.25	3.30	4.90	5.00	5.25	5.55	5.45
191	2.40	3.25	3.50	3.35	3.40	3.50	2.00	2.00	2.10	2.30	2.30
192	0.60	0.75	0.65	0.70	0.75	0.75	0.75	0.95	1.10	1.15	1.10
189	0.95	1.25	1.45	1.40	1.35	1.25	0.50	0.45	0.65	1.15?	0.60
190	0.50	0.70	0.65	0.65	0.75	0.70	0.70	0.75	0.75	0.75	0.70
197	1.10	1.35	1.45	1.45	1.65	1.70	0.80	0.85	0.90	0.95	1.00
198	0.95	1.00	1.10	1.10	1.30	1.20	1.25	1.20	1.00	1.25	1.25
193	1.95	2.50	2.75	2.90	3.00	3.00	3.20	3.50	3.60	3.80	3.75
194	0.60	0.95	1.00	0.80	0.95	0.95	1.50	1.55	1.60	1.70	1.70

$\text{BaCl}_2$  or  $\text{KCl}$ , heated at various temperatures, and filtered. The filtrate was titrated in the usual manner with 0.02 N KOH. To save space, table 4 gives data on one temperature and on one series of soils only. It will be seen that the rise in temperature decreased the speed of reaction, or increased it in

a negative sense. What apparently happened was: Heat causes coagulation in colloid reactions; which in turn decreases the specific surface and thus decreases reactivity; consequently, the placement process slowed down.

Gedroiz (3, p. 21) states that the reaction of mutual exchange of cations is instantaneous. In his experiments the amount of cations replaced (as calculated from the Ca) does not differ from the time of contact. The figures on the titration in tables 2 and 5 and curves 1, 2, and 3 show that there is a gradual increase in replacement with the time of contact. The reaction comes to an equilibrium after 7 to 10 days of contact. More prolonged contact did not increase the amount of hydrogen replaced. The curves also show that the greatest replacement takes place within the first 24 hours.

When table 5 is examined more closely, several interesting features appear. First, we note that in the plot soils the speed of replacement with the  $\text{BaCl}_2$  solution is invariably greater than with the KCl solution. On the other hand, in the Chenango series the greater speed of replacement with the  $\text{BaCl}_2$  solution is true only in several of the samples; a few samples show practically the same speed of replacement for both the  $\text{BaCl}_2$  and KCl solutions. There are a few samples with a distinct tendency toward a greater speed of replacement with KCl solution. From knowledge of the adsorption coefficients and of the replacement of the various cations, one should expect the Ba ion, a bivalent ion, to replace other cations faster than K ion would. This theoretical background finds support in the analyses of the data on the plot soils.<sup>7</sup> But why the inconsistency with the Chenango soils? Thus far no satisfactory explanation can be offered. Preliminary experiments in an effort to solve the problem pointed toward a survey of the capacity of the various soils for replacement and an inventory of the cations present in the complex capable of exchange.

Table 5 also shows that not all of the soils possess the same speed of replacement; this feature has been pointed out in connection with the discussion of table 2. There is, however, another angle of this phenomenon; namely, the relationships arising from reactions governed by the nature of the colloid substance involved.

As previously mentioned, it is the colloid fraction of the soil that is responsible for the reactions in base exchange. The mode of the reactions naturally depends upon some of the fundamental ideas of colloid chemistry, and a few preliminary remarks may help to throw more light on the subject of speed of reactions.

One of the chief characteristics of colloid reactions is their surface nature. With an increase in the degree of dispersion of particles or, as Ostwald (12) prefers to call it, "the specific surface," the reactivity of the dispersed phase

<sup>7</sup> It may be of interest to note here that data with  $\text{NH}_4\text{Cl}$  solution seem to show that the coefficient of adsorption and replacement of  $\text{NH}_4$  ion follows the K ion; this is in accord with the octet theory of valence as presented by Langmuir; see Jour. Amer. Chem. Soc., v. 42, p. 274; v. 38, p. 221; v. 40, p. 1361.

increases. If, for the sake of illustration, the cubical structure of particles is assumed, table 6 (taken from Ostwald) gives an idea of the increase in surface.

The nature of the plot soils is such that in 11A the colloids involved are more dispersed than in the other soils because of unsaturation. A water extract of this soil is turbid; showing that the H ions peptized the colloids, increasing its specific surface and hence its reactivity.

TABLE 6  
*Increase in the surface of a cube with progressive decimal subdivision*

LENGTH OF ONE EDGE	NUMBER OF CUBES	TOTAL SURFACE	SPECIFIC SURFACE
1 cm.	1	6 sq. cm.	6
1 mm.	$10^3$	60 sq. cm.	$6 \times 10^1$
0.1 mm.	$10^6$	600 sq. cm.	$6 \times 10^2$
0.01 mm.	$10^9$	6000 sq. cm.	$6 \times 10^3$
1.0 $\mu$	$10^{12}$	6 sq. m.	$6 \times 10^4$
0.1 $\mu$	$10^{15}$	60 sq. m.	$6 \times 10^5$
0.01 $\mu$	$10^{18}$	600 sq. m.	$6 \times 10^6$
1.0 $\mu\mu$	$10^{21}$	6000 sq. m.	$6 \times 10^7$
0.1 $\mu\mu$	$10^{24}$	6 hectares	$6 \times 10^8$
0.01 $\mu\mu$	$10^{27}$	60 hectares	$6 \times 10^9$
0.001 $\mu\mu$	$10^{30}$	6 sq. km.	$6 \times 10^{10}$

TABLE 7  
*Suction force of limed and unlimed soil*

SOIL NUMBER*	SUCTION FORCE: RISE OF MERCURY COLUMN
	cm.
7A	28.1
7B	25.0
11A	24.6
11B	21.5
10A	28.0
10B	25.6
12A	21.9
12B	18.1

\* For fertilizer treatments see pages 185-186 of this article. The A and B plots are treated identically, but receive applications of from 2000 to 4000 pounds of lime every 5 years.

The effect of the degree of dispersion is brought out more clearly in the time rate curves. (Figs. 1, 2, and 3). They resemble true adsorption curves as outlined by Freundlich (1), being in reality replacement curves; the adsorbed hydrogen ions arrange themselves on the surface and, if other cations are present, have to share the space with them. For this reason the more acid soils are dispersed more highly and react with a greater speed. The parallelism of the curves shows that the various soils possess the same type of colloid substance, varying only in degree of dispersion. It is easy to predict from the time rate curves the so-called "colloidality" of the soil.

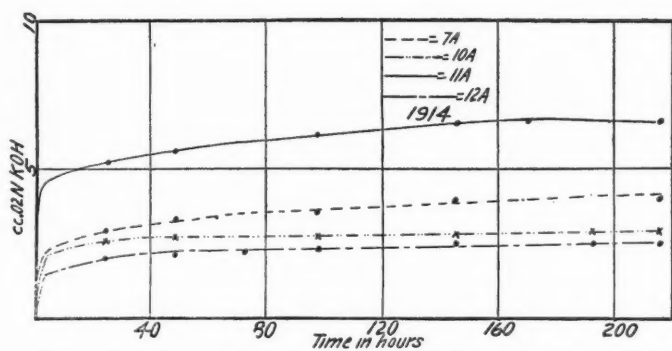


FIG. 1. TIME RATE CURVES OF SOILS 7A, 10A, 11A, AND 12A FOR 1914

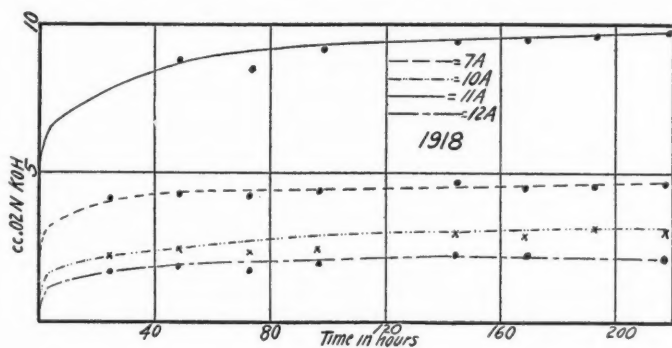


FIG. 2. TIME RATE CURVES OF SOILS 7A, 10A, 11A, AND 12A FOR 1918

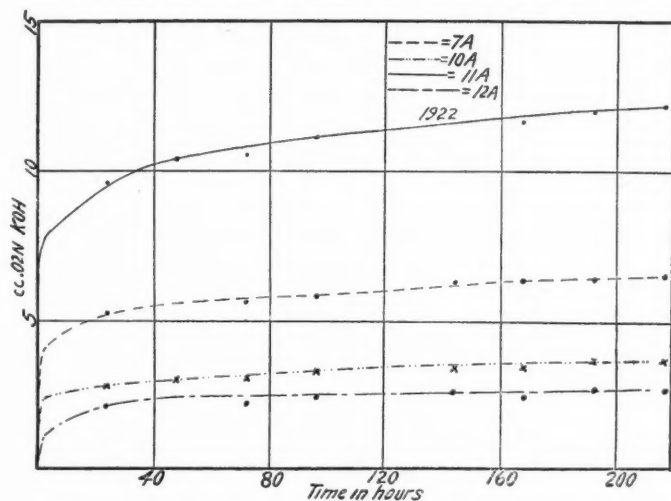


FIG. 3. TIME RATE CURVES OF SOILS 7A, 10A, 11A, AND 12A FOR 1922



That the colloidalilty of the soil is increased with the increase of the replaceable H ions has been pointed out in the first paper of this series (9). Table 7 gives the data on the suction force of limed and of unlimed soils. This suction force is an expression of the colloidalilty of the soil.

The lime as a coagulating agent, therefore, depresses the degree of dispersion of the soil colloids whereas the hydrogen peptizes the colloids, increasing their reacting surface.

The relation of the degree of dispersion brought about by increased acidity to lime requirement of soil will be the subject of the next paper.

#### SUMMARY

The subject of the rôle of the soil complex capable of base exchange or of the colloid fraction is analyzed and discussed.

The problem of soil acidity is reduced to the question of state of saturation and unsaturation of the soil complex capable of base exchange.

Experiments were conducted to determine quantitatively the amount of hydrogen ions present in the soil complex.

It is shown that the measurements of the H ion content in a water extract of soils add very little to our knowledge of the state of saturation or unsaturation. They give only an idea of the free acid present.

The cycle of replacement of H ions in the presence of other cations is discussed; the effect of this cycle on the Al-ions is presented.

The potential acidity, or the replaceable H ions, of some of the soil fertility plots of the New Jersey Experiment Station was determined quantitatively.

The speed of cation replacement is linked with the colloidal nature of the soils investigated.

Data presented show the effect of concentration of replaceable cations on the speed of replacement in the colloid fraction of the soil.

Temperature effects bring about a coagulation of the colloids and thus a slowing down of the replacement reactions.

Time rate data show that replacement is speeded up by longer contact within certain limits.

The time rate curves show typical adsorption curves. They point toward the colloidalilty of the soils, corroborating the determinations made on the colloidalilty of the soil by the suction force method.

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## A STUDY OF SOME OF THE FACTORS AFFECTING THE SUPPLY OF MOISTURE TO CROPS IN SANDY SOILS<sup>1</sup>

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The sandy soils of Wisconsin, as well as of other states, present a problem of no small dimensions to those who are actively engaged in utilizing them for the purpose of crop production. This fact may be emphasized more concretely by stating that approximately six million acres,  $\frac{1}{3}$  of the total area of the state, are recognized as sandy soils. Many areas of considerable size are very densely populated; some are undergoing development; and others are still in the virgin state. As the acreage of these soils under cultivation increases, the greater, from an economic point of view, becomes the problem of profitable crop production.

Among the factors upon which successful crop production depends is that of fertile soil. To qualify as such, the soil should first, possess a favorable moisture supply; second, contain sufficient air; third, possess the quality of good tilth; fourth, contain a good supply of available plant-food elements; and fifth, be free from harmful influences. The two most important of these as related to sandy soils are the first and fourth, the effectiveness of the latter being largely dependent upon the former.

The mean annual rainfall for Wisconsin, as cited by Whitson and Baker (30), is 31 inches, about half of which comes in May, June, July and August, and nearly 70 per cent from April to September inclusive. This amount with its favorable distribution normally supplies the needs of crops over the state as a whole.

The utilization of the rainfall by crops, however, is closely related to the water-holding capacity of the soil, which, in turn, is governed largely by its texture and structure. Sandy soils, as a group, are coarse-textured, open soils of relatively low water-holding capacity. The effect of this is all too frequently reflected in materially decreased yields of crops grown upon them.

<sup>1</sup> Part of a thesis submitted to the Faculty of the Graduate School, University of Wisconsin, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

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## PURPOSE

The three most important classes of sandy soils from the standpoint of their distribution are medium sand, fine sand and sandy loam. It is the purpose, therefore, of this investigation to study some of the factors affecting the supply of moisture to crops in these three soil classes.

## REVIEW OF LITERATURE

Reports on the results of parallel investigations are few. Many studies have, however, been made on closely related phases, some of which may well be considered.

The rate and amount of percolation of water has an important bearing upon the utilization of rainfall by crops. King (16) in his irrigation experiments on Plainfield sand shows that an application of 0.75 inch of water on sand containing an initial moisture content of 9.17 per cent reached a depth of 3 feet during 21 hours, and emphasizes the fact that when much more than one inch of water is applied at once, percolation is likely to occur. Suprunenko (28) notes a somewhat less rapid rate. Harris and Turpin (13) find that 0.1 inch of rainfall on a loam under dry-farming conditions cannot be detected in moisture determinations soon after, but within a short time a 0.5 inch fall increases the moisture content to a depth of 6 feet. Burr (8) finds that an inch of rain falling upon a very dry surface of fine sandy loam will seldom penetrate to a depth greater than six inches. King (14, 15), working with 10-foot columns of sands and of a sandy loam, shows that water in moist soils establishes itself in a gradient, the least at the top and the most at the bottom of the column, regardless of the previous distribution. Briggs (3) and Briggs and Lapham (4) find the most moisture nearest the source of supply and the least, farthest away.

Irrigation studies by Loughbridge (20) show the downward movement of water through a sandy loam to be very irregular in its rate and in the amount retained at various depths.

Columns of sandy loam, 7 feet long, with no evaporation, are shown by King (15) to retain 23.27 inches of water after draining 60 days.

The influence of soil type upon percolation is shown by Fraps (9) in three years work with 24-inch columns of four uncultivated heavy and sandy soils. The average annual rainfall during the period was 33.45 inches. He finds the average percolation for the three years from the clay and clay loam group to be twice as much (12.72 inches) as that from the sandy loam group (6.36 inches). The results are explained by the fact that the sandy group lost much greater quantities of water by evaporation than did the clay group.

It has been shown by Principi (25) and Fraps (9) that evaporation is most rapid from materials which have the largest pore spaces; the former (25) demonstrates that evaporation remains almost the same whether it arises from a free water surface or from thin films covering the particles of the wet material. Mohr (24) states that evaporation at the beginning is greater from wet soil surfaces than from a free water surface, but finally decreases until the reverse order is obtained. Harris and Robinson (12) and Wollny (31) on the other hand find a gradual increase in evaporation from graded sand particles as the size decreases.

The evaporation from the moist surfaces of Janesville loam and Norfolk sand for a season is shown by King (17) to be 25.26 and 27.27 inches, respectively. He (16) also finds a much greater evaporation of water from a free water surface than from that supplied by rainfall for the corresponding period. Meyer (23) states that about 50 per cent of the evaporation from land occurs within three days after precipitation.

Buckingham (7), studying the drying of soils under arid and humid conditions, finds a much greater rate of evaporation under the former during the first four days, but the total loss of moisture becomes and remains greater under the latter conditions.

That soils possess a great attractive and adhesive force for water has been established by Bouyoucos (2). The comparative magnitude of these forces in different soils is expressed by Schull (27), Briggs and Shantz (6), and Briggs and McLane (5).

Wollny (31) and Krakov (18) show that capillary rise in coarse-textured soils is less than in fine, but that the rate of rise is at first directly proportional to the coarseness of the particles. Later, however, the reverse is true.

The idea that capillarity plays a very important rôle in supplying moisture to crops is gradually being discredited. Tulaykov (29), Gardner (10), Burr (8), Buckingham (7), and Lee (19) show the capillary lift of sandy soils to be low. The results of the work of Lynde and Dupre (21) on soil separates are likewise in close agreement.

Rotmistrov (26) concludes that water percolating beyond a depth of 16 to 18 inches in a clayey soil returns to the surface only by means of the roots of plants, and all waters not so utilized go down into the deeper layers of the soil, moving at a yearly rate of about seven feet.

He says: "As regards the circulation in an upwards direction, there exists a wrong impression, which our literature has almost made a household word. It is maintained that water can rise to the surface from the *deep* layers by capillary action. I shall not name the authors who maintain this theory—they are too numerous; but I do not know of a single author who could prove this proposition. Of course, by 'deep' soil layer almost any measurement may be understood: 50 or 200 cm., 35 or 70 feet. . . . Consequently by the word 'deep' must be understood those layers into which the roots of cultured plants do not strike."

#### EXPERIMENTAL CONDITIONS

A part of the experimental work was performed on soils transferred from the field into cylinders placed under somewhat different climatic conditions; the remainder, on field plots under nearly uniform climatic conditions.

#### *Cylinders*

Work with cylinders was conducted as three experiments:

Experiment I, begun in 1916, included a series of 27 cylinders at Madison; Experiment II, begun in 1920, a series of 6 cylinders at Madison; Experiment III, begun in 1922, a series of 18 cylinders at the Experimental Farm at Hancock, Wisconsin.

The heavy galvanized iron cylinders are 18 inches in diameter. Each one is provided with a  $\frac{1}{2}$ -inch drainage pipe,  $\frac{1}{2}$ -inch above the bottom. A small amount of gravel was placed over the openings of the drain pipes to prevent them from clogging with soil. All cylinders in the second experiment at Madison and the third experiment at Hancock (figs. 2 and 3) are 53 inches in height and are sunk 18 inches apart, with their tops flush with the surface of the ground, the former within a screened inclosure. In the first experiment (fig. 1) cylinders 1, 10, and 19 are 27 inches; 4, 13, and 22, are 78 inches; and the remainder, 53 inches in height. In setting these cylinders, 3 trenches—34.5 feet in length—were dug to depths corresponding to the heights of the cylinders. To insure adequate drainage, a tile drain was laid beneath the bottom of the trench in which the tallest cylinders were to be placed. Vitrified sewer tile, 22 inches in diameter, were then set in a vertical position flush with the surface of the ground so that the bells of the exposed joints were 18 inches apart in one direction and 12 inches in the other. That portion of the trenches not occupied by the tile was filled with the excavated soil. The cylinders, which were within a screened inclosure, were then set within the appropriate tile and later filled with soil.

Experiment IV included 3 series of plots, of 3 plots each, which were established on farms in the vicinity of Hancock, Wisconsin, during the early spring of 1921. (Fig. 4.) The medium sand (100 series) and the sandy loam (300 series) plots were laid out in a north and

south direction; the fine sand (200 series) plots lie in an east and west direction. The medium sand series is level throughout; the fine sand series slopes gently to the west; and plot 2 of the sandy loam series slopes gently to the north to plot 3, which has slightly less elevation

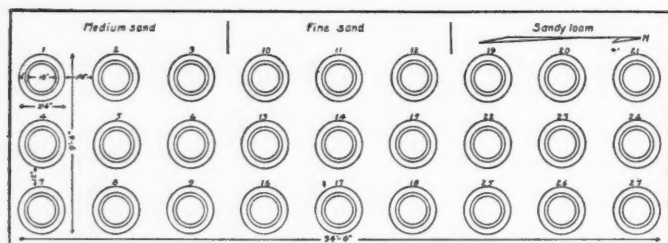


FIG. 1. ARRANGEMENT OF CYLINDERS IN EXPERIMENT I AT MADISON, CONTAINING MEDIUM SAND, FINE SAND, AND SANDY LOAM

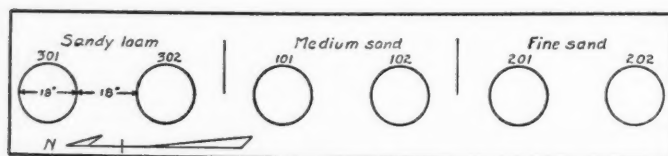


FIG. 2. ARRANGEMENT OF CYLINDERS IN EXPERIMENT II AT MADISON, CONTAINING MEDIUM SAND, FINE SAND, AND SANDY LOAM FROM EXPERIMENTAL PLOTS NEAR HANCOCK

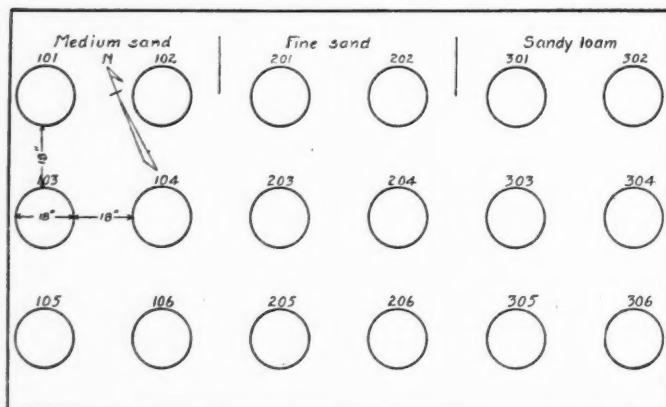


FIG. 3. ARRANGEMENT OF CYLINDERS IN EXPERIMENT III AT THE HANCOCK EXPERIMENTAL FARM, CONTAINING MEDIUM SAND, FINE SAND, AND SANDY LOAM FROM EXPERIMENTAL PLOTS NEAR HANCOCK

than plot 1. The individual plots were 2 rods square—enclosing an area of  $\frac{1}{16}$  of an acre. They were separated by  $\frac{1}{2}$ -rod division strips and surrounded by a  $\frac{1}{2}$ -rod border strip. A general view of these series is shown in plate 1.

### Soils

The soils employed in all experiments belong to the Coloma series and are recognized as Coloma sand, Coloma fine sand, and Coloma sandy loam in the United States Bureau of Soils classification.

The medium sand consists of loose sand of medium texture, very light brown, to a depth of 7 inches. At this point the color changes rather abruptly to a brownish-yellow for a few inches and then grades into a golden yellow to a depth of at least 40 inches. The texture is quite uniform.

The surface soil of the fine sand consists of a light yellow, loose sand of fine texture to an average depth of 8 inches, where it gradually grades into a darker yellow, slightly more compact, fine sand. At an average depth of 24 inches the color changes to a golden yellow, which persists to 40 inches.

The sandy loam consists of a brown, loamy, medium sand to a depth of eight or nine inches. At this depth it grades into a brownish-yellow, loamy sand and becomes somewhat coarser in texture to a depth of 24 inches. From 24 to 36 inches the subsoil consists of a yellowish-brown, sticky, sandy loam containing some stones and boulders, beneath which the soil becomes somewhat more open

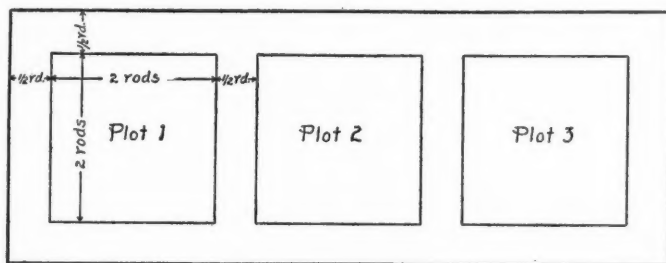


FIG. 4. ARRANGEMENT OF PLOTS IN EXPERIMENT IV IN EACH OF THE THREE SERIES OF PLOTS NEAR HANCOCK

The soils used in experiment I at Madison were collected<sup>3</sup> before the plot areas were established and consequently vary somewhat in mechanical composition from the soils used in experiments II and III which were collected from the plot areas of experiment IV. A mechanical analysis was made in duplicate from well composited samples of each soil, according to the method used by the Bureau of Soils of the United States Department of Agriculture. The average results are given in tables 1 and 2.

Inspection of the above data shows the medium sand and the fine sand to be within their prescribed limits. The sandy loam, however, contains less than the lower limit of 20 per cent of silt and clay.

The organic matter content in table 1 was determined by multiplying the organic carbon by the factor 1.724. These determinations were made in duplicate. The Truog test for soil acidity showed all soils to be from slightly to mediumly acid.

<sup>3</sup> Collected by Professor E. J. Gaul.

TABLE 1

*Mechanical composition, organic matter and moisture equivalent of medium sand, fine sand, and sandy loam used in experiment I in cylinders 1-27 at Madison*

SOIL CLASS	DEPTH	FINE GRAVEL	COURSE SAND	MEDIUM SAND	FINE SAND	VERY FINE SAND	SILT	CLAY	TOTAL	ORGANIC MAT- TER	MOISTURE EQUIVALENT
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
Sand.....	Surface	1.88	6.57	28.89	43.63	8.12	6.60	4.17	100.86	1.00	5.89
	Subsoil	2.15	6.54	31.46	44.64	5.87	5.97	3.61	100.24	0.40	4.14
Fine sand....	Surface	0.28	1.20	15.08	67.30	9.03	3.46	3.81	100.16	0.56	4.24
	Subsoil	0.03	0.99	13.30	73.13	9.42	1.69	2.54	101.10	0.24	2.24
Sandy loam...	Surface	2.27	2.60	13.28	43.69	21.02	14.12	4.11	101.09	1.08	8.28
	Subsoil	5.18	4.53	17.88	38.96	18.78	10.78	3.74	99.95	0.29	8.64

TABLE 2

*Mechanical composition of soils used in experiments II, III, and IV, from field plots near Hancock*

DEPTH	FINE GRAVEL	COURSE SAND	MEDIUM SAND	FINE SAND	VERY FINE SAND	SILT	CLAY	TOTAL
inches	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Coloma sand</i>								
0-6	0.29	16.28	40.07	29.14	4.32	5.80	3.88	99.78
6-12	0.40	20.58	42.74	24.76	3.71	4.85	3.60	100.64
12-18	0.45	17.86	42.60	28.69	3.07	4.29	3.54	100.50
18-24	0.40	20.15	44.28	27.05	2.32	3.08	2.89	100.17
24-30	0.47	19.04	41.88	30.06	3.13	2.48	2.59	99.65
30-36	0.37	19.67	42.18	30.26	3.01	2.33	2.25	100.07
36-40	0.37	15.77	40.13	34.04	4.96	2.66	2.24	100.07
<i>Coloma fine sand</i>								
0-6	0.11	7.32	27.31	51.53	5.92	4.86	4.66	101.71
6-12	0.19	7.31	25.47	52.36	6.05	4.65	3.67	99.70
12-18	0.17	7.36	24.96	54.41	5.22	3.96	3.45	99.53
18-24	0.16	8.11	25.56	54.17	5.71	2.89	3.55	100.24
24-30	0.10	6.33	23.08	58.86	6.60	2.00	3.07	100.04
30-36	0.30	8.46	26.62	55.30	6.34	1.57	2.32	100.91
36-40	0.16	6.36	24.57	59.91	5.81	1.33	1.84	99.58
<i>Coloma sandy loam</i>								
0-6	0.30	9.92	20.82	36.41	13.69	14.08	4.85	100.07
6-12	0.27	8.79	20.61	40.52	13.48	11.71	4.37	99.75
12-18	0.49	11.77	23.77	38.37	12.38	9.17	4.10	100.05
18-24	0.30	12.65	24.70	36.71	11.62	7.90	6.26	100.14
24-30	0.31	12.18	22.57	35.20	13.67	9.02	7.76	100.71
30-36	0.64	14.49	26.12	31.90	10.78	8.64	7.61	100.18
36-40	0.68	13.51	25.63	33.05	11.60	7.72	7.61	99.80



The moisture equivalents in table 1 were determined in duplicate according to the method developed by Briggs and McLane (5).

In collecting the soils for the cylinder experiments, the different strata were taken separately and placed in their natural order in the cylinders. During the process of filling, the soils were tamped to approximate field conditions of compaction.

#### *Rotation of Crops*

In the spring of 1917 a 3-year rotation of corn, oats, and medium red clover was started in connection with experiment I. A crop of clover was harvested that year, but during the following winter and each succeeding one, the clover seeding was killed and soybeans were substituted in its place. Each crop was grown each year.

In experiment II one rotation of corn, oats, and soybeans was completed, one crop being grown each year.

A rotation of corn, rye and soybeans was followed in experiment III, each crop being grown on each class of soil each year.

When the plots in experiment IV were established, a 3-year rotation of corn, oats, and clover was planned, but was changed in 1922 to corn, rye, and clover. Clover was seeded with oats in 1921 but as it did not survive the winter following, soybeans took its place in 1922.

#### *Fertilizer Treatment*

An attempt was made to supply sufficient plant-food materials to the soils so that the moisture supply, as determined by the texture of the soil, would be the limiting factor in crop production. The fertilizers were applied broadcast and were well worked into the surface in amounts sufficient to meet the requirements of each crop. Group limestone was applied at the required rates as indicated by the Truog test for soil acidity.

#### *Moisture Determinations*

Samples of each of the three classes of soils were collected in experiment IV at varying intervals for moisture determinations, of which over 1200 were made during the 3-year period. Determinations were made on each individual plot. Samples at 6-inch intervals were taken to a depth of 36 inches, and at a 4-inch interval, to 40 inches. The composites from which the determinations of each were made were secured from three different portions of the plot. The samples were taken by means of a King soil sampler.

The first four sets of determinations in 1921 were made on the entire composite for each depth in large tin boxes with tightly fitting covers. Between 400 and 500 gm. of soil were used, the weighing being made on a Troemner solution balance. Later, however, small portions—about 50 gm.—of the composites were placed in small aluminum weighing boxes with tight fitting covers and the weighings made on an analytical balance.

The samples were dried at 106° to 108°C. in ovens placed above a four-burner Perfection oil stove. A thermometer was inserted through the side of each oven from which the temperature of the ovens was observed. The flames were regulated to hold the ovens within a 2-degree variation of temperature.

### *Rainfall*

During the growing season of 1917 a record was kept of the amount of rain received within the screened enclosure at Madison. It so closely agreed with the record of the United States Weather Bureau that the observations in the enclosure were discontinued.

At the Hancock Experimental Farm the amount of rainfall was secured from the farm meteorological records, and that for the outlying series of plots was secured from the farm records in 1921 and from rain gauges on each series in 1922 and 1923.

The results of field observations and of moisture determinations indicate that precipitation of less than 0.3 inch coming as an individual shower or as an accumulation over a two- or three-day period has practically no beneficial effect on the crops on these sandy soils. Figures 5 and 6 are, therefore, designed to show the amount and distribution of precipitation, during the growing season, of 0.3 inch or more which fell during a one-, two-, or three-day period. The rainfall on the Coloma fine sand plots is practically identical with that at the Experimental farm. The graphs of the former, therefore, serve also as those of the latter.

## RESULTS

### *Yields*

In order that the yields of crops in the four experiments may be easily compared, they have been reduced to average tons and bushels of each crop produced. In computing the average yields of grains, it has been assumed that the grain is that portion of the crop from which the farmer realizes the larger proportion of his cash income. The average yields of the grains, therefore, represent the returns the farmer would have obtained in growing the crops for that purpose during the years over which the various experiments were conducted. These averages are shown in tables 3, 4, 5, and 6.

One of the outstanding facts shown in tables 3 and 4 is that of the extremely low average yield of oats, especially when grown on medium and fine sand. This agrees with the generally accepted belief that oats cannot be grown profitably on the lighter sandy soils.

The average corn yields on these soils are low. Table 3 shows a 7-year average of 6.8, 11.3, and 18.0 bushels per acre for medium sand, fine sand, and sandy loam respectively, whereas table 6 shows a somewhat higher 2-year average of 21.1, 13.2, and 28.7 bushels for the same classes of soil. The marked depressed yield of 13.2 bushels on the fine sand as compared to 21.1 bushels on medium sand is not in keeping with the yields in the other experiments, but

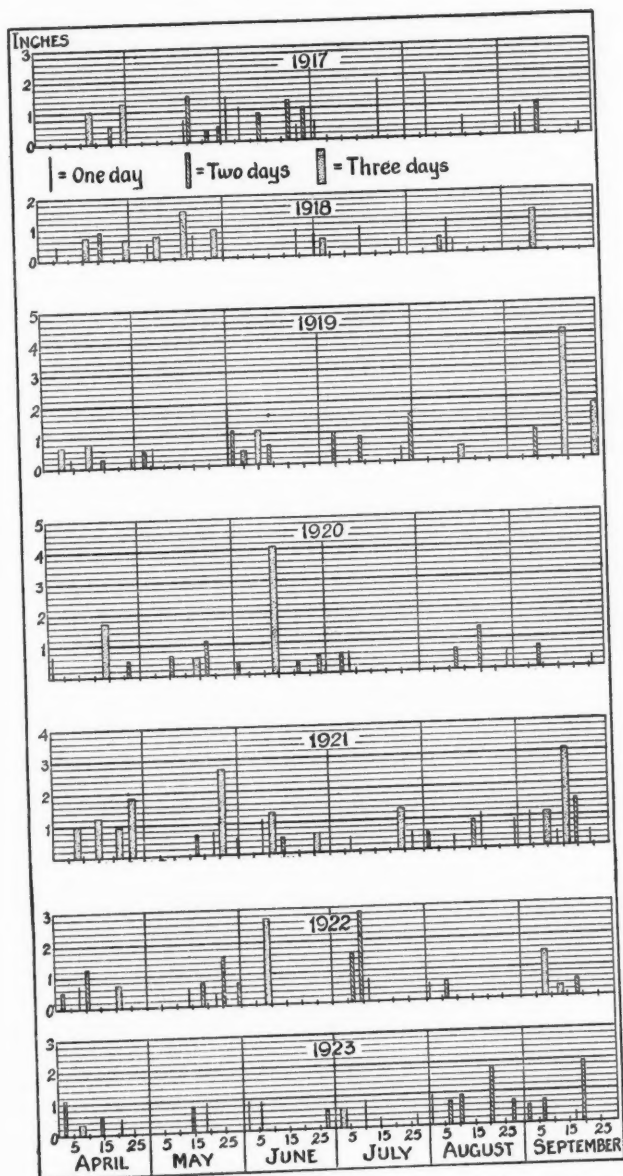


FIG. 5. AMOUNT AND DISTRIBUTION OF RAINFALL OF 0.3 INCH OR MORE OCCURRING WITHIN 1-DAY, 2-DAY, OR 3-DAY PERIODS DURING THE GROWING SEASON AT MADISON 1917-1923

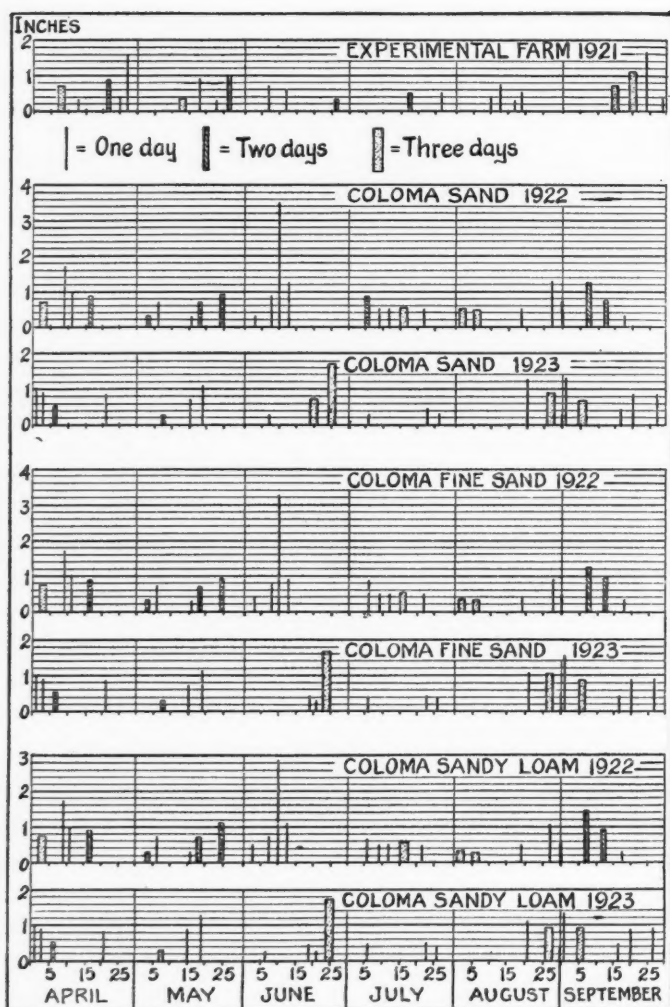


FIG. 6. AMOUNT AND DISTRIBUTION OF RAINFALL OF 0.3 INCH OR MORE OCCURRING WITHIN 1-DAY, 2-DAY, OR 3-DAY PERIODS DURING THE GROWING SEASON AT THE HANCOCK EXPERIMENTAL FARM AND THE PLOTS NEAR HANCOCK

The rainfall for Coloma fine sand is also the rainfall at the Experimental Farm during 1922 and 1923.

as yet it has been impossible to determine what condition or set of conditions produced it. By selecting the years in which the highest yields of corn were obtained in experiment I, it is found that the medium sand produced a 2-year

TABLE 3

*Average yields of corn, oats, soybeans, and clover, from experiment I, grown on medium sand, fine sand, and sandy loam in cylinders 1-27, at Madison 1917-1923*

CROP	MEDIUM SAND		FINE SAND		SANDY LOAM	
	Total weight of air-dried material produced on three cylinders from 1917 to 1923 inclusive	Average yearly yield per acre	Total weight of air-dried material produced on three cylinders from 1917 to 1923 inclusive	Average yearly yield per acre	Total weight of air-dried material produced on three cylinders from 1917 to 1923 inclusive	Average yearly yield per acre
	<i>pounds</i>		<i>pounds</i>		<i>pounds</i>	
Corn 7 years:						
Stover.....	128,162.5	3.05 T.	112,560.3	2.64 T.	143,489.8	3.42 T.
Grain.....	9,997.2	6.8 bu.	16,631.3	11.3 bu.	26,483.9	18.0 bu.
Total.....	138,159.7	3.29 T.	129,191.6	3.07 T.	169,973.7	4.04 T.
Oats 7 years:						
Straw.....	36,498.7	0.87 T.	41,230.8	0.98 T.	61,429.4	1.46 T.
Grain.....	2,107.8	3.1 bu.	6,914.5	10.3 bu.	9,471.0	14.4 bu.
Total.....	38,606.5	0.92 T.	48,145.3	1.15 T.	70,900.4	1.68 T.
Soybeans 6 years:						
Straw.....	54,741.3	1.52 T.	55,513.5	1.54 T.	59,569.0	1.65 T.
Grain.....	8,829.2	8.2 bu.	8,068.7	7.4 bu.	9,357.8	8.6 bu.
Total.....	63,570.5	1.76 T.	63,582.2	1.76 T.	68,926.8	1.91 T.
Clover 1 year:						
Hay.....	11,562.5	1.92 T.	16,441.8	2.74 T.	14,061.8	2.34 T.
Average pounds produced per acre during seven years	3,949		4,364		5,010	

TABLE 4

*Average yields of corn and soybeans from experiment II grown on medium sand, fine sand, and sandy loam at Madison, 1921 and 1923*

CROP	MEDIUM SAND		FINE SAND		SANDY LOAM	
	Total weight of air-dried material produced on two cylinders in 1921 and 1923	Average yearly yield per acre	Total weight of air-dried material produced on two cylinders in 1921 and 1923	Average yearly yield per acre	Total weight of air-dried material produced on two cylinders in 1921 and 1923	Average yearly yield per acre
	<i>pounds</i>	<i>tons</i>	<i>pounds</i>	<i>tons</i>	<i>pounds</i>	<i>tons</i>
Corn 1 year:						
(Stover).....	6,202.5	1.55	8,871.6	2.22	13,116.0	3.27
Soybeans 1 year:						
(Hay).....	5,444.8	1.36	5,708.6	1.43	7,269.1	1.82
Average pounds produced per acre during two years.....	2,911.8		3,645.0		5,096.2	

average of 23.8 bushels, whereas the fine sand and sandy loam produced a 3-year average of 26.4 and 42.0 bushels per acre, respectively. On the basis of the 7-year period, these better yields may be expected about 4 out of 10 years. In 1922, in experiment IV, corn made a good yield for ensilage or grain. At 70 cents a bushel the returns from medium sand, fine sand, and sandy loam were \$29.40, \$18.20, and \$39.90 per acre, respectively.

Soybeans as a seed crop, with average yields for 7 years of 8.2, 7.4, and 8.6 bushels per acre (table 3) do not pay. On the other hand, fairly normal

TABLE 5  
*Average yields of corn, rye, and soybeans from experiment III grown on medium sand, fine sand, and sandy loam in the cylinders at the Hancock Experimental Farm, 1922-1923*

CROP	MEDIUM SAND		FINE SAND		SANDY LOAM	
	Total weight of air-dried material produced on two cylinders from 1922-1923	Average yearly yield per acre	Total weight of air-dried material produced on two cylinders from 1922-1923	Average yearly yield per acre	Total weight of air-dried material produced on two cylinders from 1922-1923	Average yearly yield per acre
	<i>pounds</i>		<i>pounds</i>		<i>pounds</i>	
Corn 2 years.:						
Stover.....	21,787.6	2.72 T.	18,385.2	2.29 T.	24,454.3	3.05 T.
Grain.....	2,335.8	4.15 bu.	4,195.0	7.49 bu.	5,081.5	9.07 bu.
Total.....	24,123.4	3.01 T.	22,580.2	2.82 T.	29,535.8	3.69 T.
Rye, 2 years:						
Straw.....	4,582.7	0.57 T.	3,686.4	0.46 T.	5,291.3	0.66 T.
Grain.....	1,933.3	8.64 bu.	1,464.2	6.53 bu.	1,686.4	7.53 bu.
Total.....	6,516.0	0.81 T.	5,150.6	0.54 T.	6,977.7	0.87 T.
Soybeans 2 years.:						
Hay.....	10,680.5	1.33 T.	15,829.6	1.97 T.	14,080.0	1.76 T.
Grain.....	.....	.....	.....	.....	.....	.....
Total.....	10,680.5	1.33 T.	15,829.6	1.97 T.	14,080.0	1.76 T.
Average pounds produced per acre during two years..	3,443.3		3,630.0		4,230.3	

yields of hay are obtained. In 1922 in experiment IV, sandy loam, produced 17.8 bushels of beans per acre whereas the medium sand and fine sand produced 6.6 and 9.6 bushels, respectively. (Table 6.)

From table 6 it is seen that in 1923 medium red clover made but 0.72, 0.43 and 0.78 tons per acre on medium sand, on fine sand, and on sandy loam, respectively. The season was extremely dry and under more normal moisture conditions the yields would have been more than doubled, as indicated by the yields of 1.92, 2.74, and 2.34 tons per acre in table 3.

A 2-year average of yields of winter rye in table 6 shows that 10.62, 9.37, and 26.16 bushels per acre were grown on medium sand, on fine sand, and on sandy

loam. This crop is one of the most reliable for sandy soils, as it matures sufficiently early to escape the longer periods of drought which frequently occur during July and August.

On the basis of yields, precipitation, texture, and moisture determinations

TABLE 6

*Average yields of corn, oats, rye, soybeans, and clover from experiment IV grown on field plots of medium sand, fine sand, and sandy loam near Hancock, 1921-1923*

CROP	MEDIUM SAND		FINE SAND		SANDY LOAM	
	Total weight of air-dried material produced on comparable plots 1921-1923	Average yearly yield per acre	Total weight of air-dried material produced on comparable plots 1921-1923	Average yearly yield per acre	Total weight of air-dried material produced on comparable plots 1921-1923	Average yearly yield per acre
	<i>pounds</i>		<i>pounds</i>		<i>pounds</i>	
Corn, 2 years:						
Stover.....	7,098	1.77 T.	6,556	1.64 T.	10,516	2.62 T.
Grain.....	2,960	21.14 bu.	1,850	13.21 bu.	4,020	28.71 bu.
Total.....	10,058	2.51 T.	8,406	2.10 T.	14,536	3.63 T.
Oats 1 year:						
Straw.....	1,420	0.37 T.	148	0.04 T.	4,384	1.09 T.
Grain.....	160	2.50 bu.	60	0.93 bu.	900	14.06 bu.
Total.....	1,580	0.39 T.	208	0.05 T.	5,284	1.32 T.
Winter rye, 2 years:						
Straw.....	2,330	0.58 T.	2,630	0.66 T.	7,280	1.82 T.
Grain.....	1,190	10.62 bu.	1,050	9.37 bu.	2,930	26.16 bu.
Total.....	3,520	0.88 T.	3,680	0.92 T.	10,210	2.55 T.
Soybeans, 1 year:						
Straw.....	980	0.46 T.	980	0.49 T.	1,770	0.89 T.
Grain.....	400	6.66 bu.	580	9.66 bu.	1,070	17.83 bu.
Total.....	1,380	0.69 T.	1,560	0.78 T.	2,840	1.42 T.
Clover 1 year:						
Hay.....	1,435	0.72 T.	855	0.43 T.	1,555	0.78 T.
Average pounds produced per acre during three years.....	2,079		1,712		3,882	

it is possible to discuss some of the factors affecting the supply of moisture to crops in these sandy soils.

#### *Effect of Texture on Utilization of Moisture in Crop Production*

On July 26, 1921 a rainfall of 0.58 inch occurred which was recorded on the 27th. Twenty-four hours after the rain had ceased moisture determinations



were made on cultivated corn plots on each soil to determine the depth to which it had penetrated. Table 7 indicates that within 24 hours the effect of the rain was slightly apparent in the 12 to 18 inch depth of medium sand, but was almost wholly confined within the 6 inch depths of fine sand and sandy loam.

August 3, eight days after the rain, another set of samples for moisture determinations were taken. Table 7 indicates that the effect of the rain in the medium and fine sands has disappeared but is evident in the 18 to 30 inch depth in the sandy loam. The increase in moisture in the 24 to 30 inch depth in the sandy loam is 5.12 per cent over that of July 27, an equivalent of 0.45 inch. Penetrating at an observed rate of 4 inches a day, the influence of this rain should have been evident in the 30 to 36 inch depth. Since the observed depth of 4 inches was made wholly within the surface soil, retardation, due to the more compact subsoil and to the demands made on the water by the growing crop, would account for this difference. The results obtained by Harris and Turpin (13) and Burr (8) from investigations with finer textured soils

TABLE 7  
*Changes in the water content of medium sand, fine sand, and sandy loam at different intervals after a 0.58 inch rain on corn plots*

DEPTH	MEDIUM SAND		FINE SAND		SANDY LOAM	
	24 hours	8 days	24 hours	8 days	24 hours	8 days
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
<i>inches</i>						
0-6	6.15	2.47	6.03	2.21	7.22	3.50
6-12	3.43	2.89	1.70	1.49	2.71	2.81
12-18	3.01	2.59	1.60	1.43	2.33	2.63
18-24	2.93	2.54	1.30	1.35	3.24	4.85
24-30	3.29	3.13	1.55	1.56	2.64	7.76
30-36	3.31	3.70	2.38	2.01	5.62	5.47
36-40	6.30	5.95	2.80	2.42	6.16	5.63

than those here employed, although not of the same magnitude, are in agreement with those reported above.

The utilization of water falling as rain in supplying the needs of crops growing upon sandy soils of low organic matter content is a function of texture. Its effect may be seen by studying the character and distribution of rainfall throughout any growing season in relation to the yields produced. The season of 1920 in experiment I has been chosen because of the drought in July. The monthly precipitation for the growing season is as follows: April, 0.43; May, 2.51; June, 5.62; July, 1.39; August, 2.61; and September, 1.12 inches.

The rainfall data for 1920 show that during the growing season there were 9 rains of 0.5 inch or more; 1 in May, 4 in June, 2 in July and 2 in August. The 4 June rains totaled 4.04 inches and fell between the 13th and 16th. According to the work of King (16) on Plainfield sand at Stevens Point, Wisconsin, the medium sand held about one inch, the remainder percolating beyond the reach of the roots of crops. That this loss is permanent is further substantiated by

Grebe (11) who, from his study of the water lifting power of very sandy forest soils, concludes that sands and very fine sands do not lift water above the water table more than 13.1 and 19.7 inches, respectively.

It is also shown in table 7 that water percolates more slowly through fine sand and sandy loam than through medium sand, the rate decreasing with the finer texture. Alway and McDole (1) have shown that 1 inch of water applied to the surface of "sandy land" with an initial moisture content of 4.9 per cent penetrated 10.3 inches at the end of 5 days.

The 2 rains that fell on July 6 to 8, totaled 1.2 inches all of which was held by the soils. A very dry period of 34 days followed, during which 0.01 inch fell on July 30, 31 and August 8, and 0.07 on August 4. On August 12 and 13, 0.64 inch; 20 and 21, 1.37 inches; and 27 to 29, 0.52 inch precipitations occurred. In September, 0.74 inch of the total 1.12 inches for the month fell during the first 9 days. A period of 34 days followed (September 10–October 13) during which 0.01 and 0.37 inch fell on September 19 and 26, respectively.

In the light of the foregoing facts concerning the distribution of rain during the season, a study of the relative utilization of moisture as influenced by texture may be made on the basis of the yields of corn.

The sandy loam gave an increase of 1146.5 pounds per acre over the fine sand and of 628.7 pounds over the medium sand. This indicates that the sandy loam is capable of retaining sufficient moisture as a reserve from the heavier rains to supply the crop more adequately with moisture during the intervening periods of light showers.

The fine sand, on the other hand, with its lower water-holding capacity, lost much more water by percolation from the heavier rains. Because the rate of penetration after a 0.5 inch rainfall is not much greater than that in the sandy loam, but nearly one-third less than in the medium sand, the fine sand has not been able to utilize the water from the lighter showers so economically as the medium sand.

In experiment II the rainfall records for 1921 show that the precipitation for the growing season is as follows: April, 5.16; May, 5.13; June, 3.52; July, 2.46; August, 3.97; and September, 7.9 inches—a total of 28.14 inches. This is exceptionally high. The distribution, with the exception of the first 22 days of July, is almost ideal. (Fig. 5.) Under these conditions the influence of texture on the utilization of moisture as indicated by yields in table 4 is shown in the order of medium sand, 1.55; fine sand, 2.22; and sandy loam, 3.27 tons of corn per acre.

During the 1923 growing season 2.59 inches of rain fell in April, 1.90 in May, 3.05 in June, 2.28 in July, 5.59 in August, and 4.36 in September—a total of 19.77 inches. Because of the light amount of precipitation in May, the soils were somewhat deficient in moisture at the time the soybeans were planted. In June, 1.92 of the 3.05 inches fell during the first 6 days, the remaining 1.13 inches falling as light showers mostly between the 25th and 28th. Another period of light rainfall occurred between July 11 and 31. The August dis-

tribution was good and so continued until September 21, followed by a dry period of 22 days. Under these seasonal conditions the medium sand utilized its moisture as well as the fine sand, which is indicated in table 4 by the yields of 1.36 and 1.43 tons of soybean hay per acre, respectively. The sandy loam, with its inability to utilize the light rains of June and July failed to give the larger proportionate yield that would have been possible under a more uniform distribution of heavier rains, as indicated by its yield of 1.82 tons per acre.

Many similar comparisons of the results of the cylinder experiments agree so closely with those above that no further comment will be made on them in this connection.

The rainfall during the growing season for oats in 1921 was unfavorable on the plots in experiment IV. Figure 6 shows that the distribution of rain in April was characterized by light showers with a 1.6 inch rain on the 27th, following which no rain fell for 14 days. From May 12 to 27, 2.71 inches fell in 6 well distributed showers. During June, 0.7 and 0.6 inches fell on the 7th and 12th, and 0.35 on the 26th and 27th, making a total of only 1.65 inches for the month. The July precipitation of 1.48 inches was less well distributed in four showers than that of June.

The effect of texture in utilizing moisture for the oats crop is shown in table 6. The sandy loam was able to hold within reach of the roots of the oats a sufficient portion of the 1.6 inches of rain in April and the 0.97 inch and 1.05 inches falling May 18, 26, and 27, to produce a yield greater than on the medium and fine sands. The effect of the marked infrequency of light showers in May and June is reflected by the low yield on the medium sand. The fine sand, on the other hand, unable to use efficiently the water of the few light showers and that of the heavier rains, produced the least. A comparison of the heights of the oats on the different soils on June 28, is shown in plate 2.

The season of 1922 was marked by a total and well distributed precipitation of 23.24 inches as compared to the 16.17 inches of 1921. A study of the rainfall distribution on the medium sand plots in figure 6 reveals a decided grouping of rains during April and May with 4 rains during the first 15 days in June, 1 of which is 3.56 inches on the 10th and the other 1.25 inches on the 13th. A period of 22 days follows without rain until May 6 following which well distributed rains of over 0.5 inch occur. Three groups of rains, which are well distributed, occur in August, and in September two groups occur during the first two weeks.

Under these conditions, 6960, 5250, and 10420 pounds of corn; 1380, 1560, and 2840 pounds of soybeans; and 2100, 2960, and 7170 pounds of rye were produced per acre on the medium sand, on the fine sand, and on the sandy loam respectively. These yields indicate that the heavy rains in April and June, were sufficiently held by the sandy loam to supply moisture to the corn crop during its vigorous growing period in July and August, whereas the lighter showers of July and August were better utilized by the medium sand than by the fine sand.

The fine sand showed but little difference from the medium sand in its supply of moisture to soybeans. The sandy loam, however, responds as in the case of the corn crop.

Rye made its maximum growth in May and June. The grouping of the rains in May and June was such that a good portion of them falling during each period was lost for the crop by percolation from the medium sand, less from the fine sand, and the least, if any, from the sandy loam. Consequently during the 22-day period of no rain in June and July, the supply of moisture in the medium sand was reduced below that of the fine sand in the root zone and was reflected in the aforementioned yields.

During the growing season of 1923 but 14.9 inches of rain fell. Its distribution is characterized by long periods of very little or no precipitation and a small number of light showers under 0.5 inch.

The effect of texture on the supply of moisture under these conditions is shown by the yields obtained. Corn produced 3090, 3156, and 4106; and rye 1420, 1620, and 3040 pounds per acre on medium sand, fine sand, and sandy loam, respectively. There is but little difference between the effect of the fine sand and medium sand in their utilization of water, especially in the case of the shallower rooting rye. The former, however, gave an increase over the latter of 200 pounds of rye.

The corn crop as it appeared on August 4 is shown in plate 3.

When the average number of pounds per acre of all crops produced during the three years is considered, it is evident that the medium and fine sands are similar in their ability to supply water to the crops, the former producing slightly more than the latter. The sandy loam, however, is most efficient, as shown in table 6.

The assemblage of the yields of the various crops produced on all of the cylinders and plots shows the average weight of dry matter produced per acre on medium sand, on fine sand, and on sandy loam to be 3327, 3588, and 4668 pounds, respectively. The difference between the productive capacity of the medium and fine sand is small. This shows that from the standpoint of production their value is nearly identical. It would be entirely feasible, therefore, in a classification in which productiveness is considered essential, to group these two classes of soils together as one.

The effect of texture on the utilization of moisture is shown further by a study of the moisture content of the soil in relation to the amount and character of distribution of the rainfall.

On July 5, 1922, moisture determinations of each class of soil were made to a depth of 2 feet. Prior to this date a 28-day period occurred which was characterized by a few heavy rains; following it, a 23-day period marked by frequent rather light rains occurred. The precipitations during the two periods are given in table 8.

Moisture determinations were made for each class of soils on June 6, the

beginning of the first period, and on July 29, the close of the second period. These results and also those for July 5 are shown in table 9.

After receiving 5.76 inches of rain, the medium sand contained 0.17 inch *less* water on July 5 than on June 6. But at the close of the second period on July 29, after receiving 2.95 inches, it contained 0.05 inch *more* water than on July 5.

The fine sand received 5.13 inches during the first period, at the close of which it contained 0.41 inch *less* water than at the beginning. On the other hand, after receiving 2.96 inches throughout the second period it contained 0.25 inch *more* water than on July 5.

TABLE 8  
*Precipitation on the medium sand, fine sand, and sandy loam plots June 6 to July 29, 1922*

28-DAY PERIOD				23-DAY PERIOD			
Date	Medium sand	Fine sand	Sandy loam	Date	Medium sand	Fine sand	Sandy loam
	<i>inches</i>	<i>inches</i>	<i>inches</i>		<i>inches</i>	<i>inches</i>	<i>inches</i>
June 8.....	0.87	0.78	0.76	July 6.....	0.83	0.86	0.66
June 10.....	3.56	3.25	2.88	July 9.....	0.51	0.51	0.52
June 13.....	1.25	0.93	1.10	July 12.....	0.52	0.51	0.52
June 27.....	0.08	0.17	0.09	July 15.....	0.03	0.03	0.04
				July 16.....	0.04	0.05	0.05
				July 17.....	0.51	0.50	0.51
				July 22.....	0.51	0.50	0.51
Totals.....	5.76	5.13	4.83		2.95	2.96	2.81

TABLE 9  
*Moisture content of the first 2 feet of medium sand, fine sand, and sandy loam plots on the dates indicated*

DATE	MEDIUM SAND	FINE SAND	SANDY LOAM
	<i>inches</i>	<i>inches</i>	<i>inches</i>
June 6.....	0.80	0.99	1.17
July 5.....	0.63	0.58	1.12
July 29.....	0.68	0.83	0.72

This shows that the medium sand and fine sand contain more water in the first 2 feet when about one-half the rainfall is distributed as light rains, than when it comes as infrequent and heavier rains. The sandy loam, however, utilizes the heavier, less frequent rains to better advantage than the lighter, more frequent rains.

#### SUMMARY

The marked depression in yields of crops on sandy soils during seasons of limited or poorly distributed rainfall has long been commonly noted. The greater portion of these soils is included in the medium sand, fine sand, and

sandy loam classes established by the Bureau of Soils of the United States Department of Agriculture. The results of numerous investigations would lead to the conclusion that there might be marked differences among these soil classes with respect to their ability to supply moisture to crops. It seemed desirable, therefore, to make a study of the moisture relationships of these soils in order to determine to what degree their moisture content, under varying seasonal distribution of rainfall, becomes a limiting factor in crop production.

1. The study was conducted as four experiments on field plots and on cylinders of each class of soil under similar and under somewhat different climatic conditions.

2. The soils used were Coloma sand, Coloma fine sand, and Coloma sandy loam, all having a low organic matter content.

3. Appropriate fertilizers were applied in amounts adequate to supply the needs of the crops so that the moisture supply, as determined by the texture of the soil, would be the limiting factor in crop production.

4. Corn, oats, clover, rye, and soybeans were the crops employed.

5. Over 1200 moisture determinations were made on the plots in experiment IV.

6. Precipitation data at Madison were secured from the records of the United States Weather Bureau, and those at Hancock, from the Experiment Farm records and from out-lying rain gauges.

7. The oats crop is not adapted to the sandy soils employed.

8. Corn for ensilage can be produced on the three classes of soil, but when it is grown for grain, should be confined to sandy loam for more profitable yields.

9. Profitable yields of corn, based on the 7 years' work in experiment I, may be expected 4 out of 10 years.

10. Rye is the small grain crop best adapted to these sandy soils.

11. As a forage crop, soybeans yield well on the three soil classes. More profitable yields of seed are grown on sandy loam, as indicated by the yields from experiment IV in 1922 when medium sand and fine sand produced 6.6 and 9.6 bushels per acre, respectively, whereas sandy loam gave a yield of 17.8 bushels.

12. The penetration of moisture on cultivated corn plots 24 hours after a 0.58 inch rain is into the 12 to 18 inch depth of medium sand, but is almost wholly confined to the 6 inch depths of fine sand and sandy loam. Eight days after the rain, its effect in the medium and fine sands has disappeared but is evident in the 18 to 30 inch depth of sandy loam.

13. Medium sand supplies crops with more moisture from light rains and showers than does fine sand or sandy loam when the precipitation comes at a time when the initial moisture content of the soils is low. The greater water-holding capacity of sandy loam enables it to store a sufficient supply from the heavier rains to produce the largest yields under the type of seasons during this investigation.

14. The difference between the productive capacities of medium and fine sand, as determined by their ability to meet the water requirements of crops over periods of 2 to 7 years, is negligible, and suggests the feasibility of grouping them together as one class in any system of classification in which productiveness is considered an essential factor.

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PLATE 1

FIG. 1. View of medium sand plots (100 series) toward the southwest corner.

FIG. 2. View of fine sand plots (200 series). Gentle slope from road toward camera.

FIG. 3. View of sandy loam plots (300 series). Gentle slope from road toward camera.



FIG. 1



FIG. 2



FIG. 3

PLATE 2

FIG. 1. Oats on medium sand plots, June 28, 1921.

FIG. 2. Oats on fine sand plots, June 28, 1921

FIG. 3. Oats on sandy loam plots, June 28, 1921



FIG. 1



FIG. 2



FIG. 3

PLATE 3

- FIG. 1. Corn on medium sand plots, August 4, 1923.  
FIG. 2. Corn on fine sand plots, August 4, 1923.  
FIG. 3. Corn on sandy loam plots, August 4, 1923.



FIG. 1

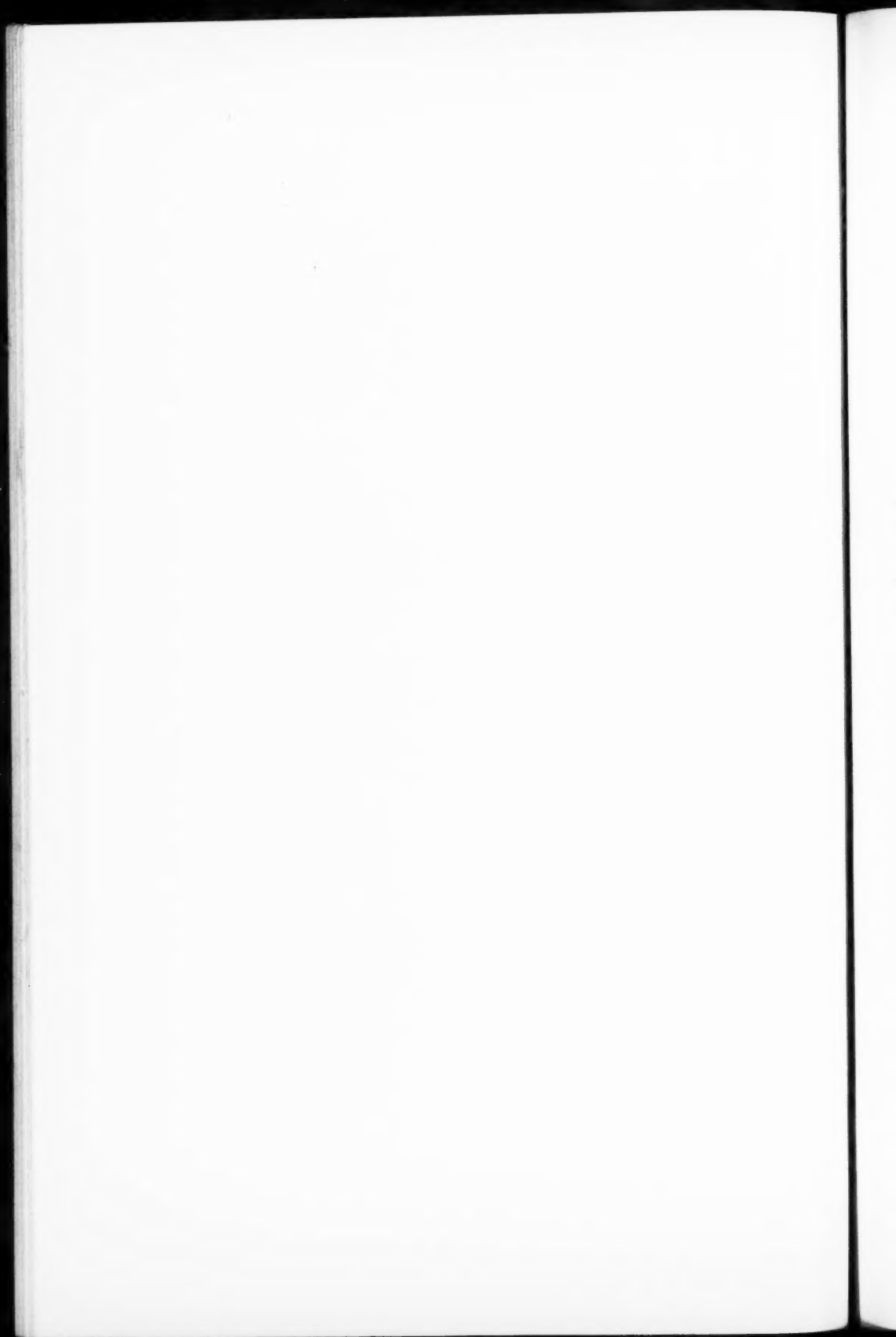


FIG. 2



FIG. 3





## THE BACTERIAL TYPES OCCURRING IN FROZEN SOIL

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### INTRODUCTION

In the course of a previous investigation by the writer (8) conducted during the season 1923-24, examinations were made of the numbers of bacteria, actinomycetes, fungi, and protozoa occurring at different depths in soil throughout the course of the winter months. Quantitative determinations were conducted at 2- to 3-week intervals from November 14 to April 21.

Although it was found that frozen soil under winter conditions such as prevail in Eastern Canada is capable of harbouring large numbers of the microorganisms studied, the results strengthened the belief that they are in a dormant state under conditions of frost.

The numbers of bacteria, developing on albumin agar plates incubated for 12 days at 20°C., remained high throughout the winter, very little variation from the count on November 14 being recorded throughout the period of frost. Although the numbers were not lessened when the soil actually became frozen, no phenomenal increases were observed which would lend support to the theory of stimulation through frost to which other observers, notably Conn (2, 3, 4) and Brown and Smith (1) would ascribe increases reported by them. Only with the advent of mild conditions was a noticeable increase in numbers observed. Parallel determinations by the direct microscopic method of Conn (7) gave no fluctuations which could be ascribed to anything apart from the high experimental error inherent in such a method. From a qualitative standpoint, the method is of greater value when some idea of the types and arrangement of the bacteria is given. In frozen soil, short rods comprised the great majority of the bacteria observed, present for the most part as single cells, the average number of individuals in each group varying from 1.33 to 1.75 during the period.

Actinomycetes, as determined by the plate method, appeared to remain more or less stationary in numbers, forming, however, a considerable proportion of the colonies found on the albumin agar plates. At a depth of 2 inches they comprised 27.2 per cent of the total bacterial colonies; at 6 inches, 34.7 per cent; and at 10 inches, 39.6 per cent.

The figures for the fungi revealed the only instance where marked increases throughout the season were recorded. Plate counts made on an agar medium

of pH = 4.0 as described by Waksman (9), showed regularly increasing numbers throughout the period of frost at the three depths studied. The significance of the plate count with fungi is different from that with bacteria and is probably related to the ability of the former to produce multiple spores. For that reason and also in the light of tests made with the other organisms, the increased counts obtained are taken to indicate increased spore production rather than enhanced vegetative activity.

Protozoa, as determined by the dilution method, decreased in numbers at the upper level throughout the frost period. At lower depths no changes were observed. After thawing at the end of winter, marked increases were found at the 2- and 6-inch levels.

With the object of gaining some insight as to the possible development of a special "winter" group of bacteria, which would tend to have a lower optimum growth temperature than a hypothetical "summer" group, determinations were made throughout the winter not only of bacteria developing at 20°, but of those developing at 3° and at 37°C. The results obtained pointed against the existence of a group of "winter" bacteria. The 20° counts were in all cases much in excess of those at 37° or at 3°, the great difference holding not only for soil in the late fall, but equally so in the case of winter soils. On the basis of the theory of special "winter" bacteria it would be expected that during the course of the cold season a change would be observed in the proportion of bacteria developing at the different temperatures. The proportion of those developing at 37° to those at 20° would be expected to decrease, whereas those developing at 3° would be proportionately more numerous. The data, however, show no downward trend at 37°, and on the other hand, no upward tendency of organisms capable of growth at 3°. The only actual marked increase in the numbers of colonies on low temperature plates occurred at the end of the period of frost. Most of the bacteria in winter soils seem incapable of development at low temperature, and further, it would seem that organisms actually capable of growth at low temperature develop, not under conditions of frost, but in unfrozen or thawed soil. In further support of this view is the fact that the only instance of increasing counts of organisms on low temperature plates occurred at 10 inches, at which depth the soil remained unfrozen.

In the course of a special study of bacteria capable of growth at low temperature (3°C.) isolated from the soil after it had been frozen for 10 weeks at 2 inches and for over seven weeks at 6 inches, 20 presumably distinct species were isolated. Of these only 1 showed better growth at 3° than at 20°, 3 showed approximately equal growth at the two temperatures, whereas the remaining 16 species all grew noticeably better at 20° than at 3°. The most abundant species belong to this last group. The results indicate that the bacteria of frozen soil are to be regarded as cold-enduring rather than psychrophilic in the true sense.

## FURTHER STUDY OF BACTERIAL TYPES

During the winter 1924-25 further studies were made of frozen soil from the same field, which had in the meantime grown a crop of corn followed by fall plowing. It was planned to continue a study of the types occurring in frozen soil with emphasis laid also on their quantitative relationships.

Samples at 2-, 6-, and 10-inch depths were taken March 13, 1925 toward the end of the period of frost, at which time any possible adjustment of types

TABLE 1  
*Bacteria found in frozen soil, March 13, 1925*

MEDIUM	INCUBATION TEMPERATURE	2-INCH	6-INCH	10-INCH
	°C.			
Albumin agar.....	37	6,800,000	6,900,000	1,450,000
Albumin agar.....	20	33,900,000	25,900,000	6,800,000
Albumin agar.....	3	2,030,000	1,570,000	550,000
Soil extract agar.....	3	2,600,000	1,730,000	380,000
Nutrient agar.....	3	6,080,000	6,500,000	1,330,000

TABLE 2  
*Bacterial types in frozen soil developing on albumin agar at 20° and 3°C.*

TYPES	20°C.			3°C.		
	Cultures isolated		Approximate number per gram soil	Cultures isolated		Approximate number per gram soil
		per cent			per cent	
Total.....	206	100.0		80	100	0
Actinomycetes.....	62	30.1	9,000,000	0	0	0
Bacteria.....	144	69.9	20,900,000	80	100	1,800,000
Micrococci (Slowly or non-liquefying).....	4	2.0	600,000	0	0	0
Short rods (Slowly or non-liquefying).....	89	43.2	12,900,000	72	90	1,600,000
Short rods (Rapid liquefiers).....	5	2.4	700,000	0	0	0
Medium to large rods (slowly or non-liquefying).....	26	12.6	3,800,000	0	0	0
Medium to large rods (Rapid liquefiers).....	4	2.0	600,000	0	0	0
Unclassified.....	16	7.8	2,300,000	8	10	200,000

through frost would have been accomplished. Triplicate plates were made of all dilutions, and parallel series of plates were prepared for incubation at 37°, 20°, and 3°C. The medium used was the albumin agar of Brown as modified by Waksman (10), though in addition soil extract agar and nutrient agar were used for plates incubated at 3°. The results of the quantitative tests are given in table 1.

As was found the previous winter the number of organisms appearing at 20° was greatly in excess of the 3° count, even after more than 2 months continuous frost. Most of the bacteria of frozen soil appear to be incapable of development at low temperature.

#### FREQUENCY OF DIFFERENT BACTERIAL TYPES IN FROZEN SOIL

A comparison was made of the frequency of the different types of organisms developing on albumin agar at 20° and at 3° respectively. For this purpose the soil at 2 and 6 inches only was considered, the sample at 10 inches being below the frost line.

Typical plates from the 2- and 6-inch sets were selected, and all colonies transferred for pure culture study. Plates showing rather fewer than 100 colonies were chosen, although in cases where rather more were present one-half of the plate only was used for isolating. Determinations of morphology and certain cultural characteristics were made, though in a number of cases where transfers showed no growth, the organisms could not, in consequence, be classified. The data presented in table 2 represent averages for the 2- and 6-inch depths.

Of the bacteria in winter soils, the short rods, non-spore-forming and with little or no liquefying power, appear to form the largest group. This type, also appears to represent most of the bacteria capable of low temperature growth (3°C.). Short rods of the rapidly liquefying type are numerically much less important. Rods of larger size are likewise less important, and belong to the class which is much inhibited by low temperature. Micrococci form a numerically insignificant group.

Actinomycetes comprise an important group of organisms, a group which under moderate temperature conditions may be physiologically as well as numerically important. On the plates at 3°C. however, they were absent, and it appears reasonable to assume that even before the soil is in a frozen state they lose their activity with the lowering temperature.

Although the medium, albumin agar, was different from that used by Conn (5) who employed gelatin in the course of an investigation into bacterial types in soil, there is a general agreement with the relative abundance of the various groups reported. Conn found that the non-sporulating, slowly or non-liquefying short rods comprised the largest group (40-75 per cent), with Actinomycetes next in point of abundance (12-50 per cent). Non-spore-forming, liquefying short rods as well as spore-formers of the *B. subtilis* group were under 10 per cent, whereas but few micrococci were observed. It would appear that these organisms from frozen soil represent a "characteristic soil flora" and the belief is further strengthened that no change to a "winter" group follows prolonged frost, the soil microflora being rather dormant.

## STUDY OF ORGANISMS DEVELOPING ON 3° PLATES

A more detailed study was made of the characteristics as well as of the relative frequency of the species appearing on the 3° plates of albumin agar, of soil extract agar, and of nutrient agar. Typical plates were selected from the 2- and 6-inch samples from which colonies were subcultured for pure culture study. In certain cases where appearance and low-power examination pointed to identical types, all were not subcultured but merely recorded.

TABLE 3

*Characteristics and frequency of bacterial species from frozen soil developing at 3°C. on nutrient agar (average of 2- and 6-inch depths)*

LABORATORY NUMBER	APPROXIMATE NUMBER PER GRAM SOIL	FORM	SPORES	MOTILITY	GRAM STAIN	CHROMOGENESIS ON NUTRIENT AGAR	GELATIN LIQUEFACTION	MILK			AMMONIA IN NUTRIENT BROTH	INDOL	NITRATES REDUCED	DEXTRSE	LACTOSE	SACCHAROSE
								Acid	Coagulation	Peptonization						
A7	3,380,000	Short rod	—	—	—	—	sl.	—	—	—	—	—	—	—	—	—
C7	1,300,000	Short rod	—	+	—	—	—	—	—	—	sl.	—	+	—	—	—
C8	380,000	Short rod	—	sl.	—	Brown	—	—	—	—	+	—	+	—	—	—
C13	100,000	Short rod	—	—	—	—	—	—	—	—	+	—	+	—	—	—
C14	100,000	Slender rod	—	+	—	Yellow-brown	—	—	—	—	sl.	—	+	—	—	—
A5	60,000	Short rod	—	+	—	—	sl.	—	+	+	+	—	—	+	—	—
C2	60,000	Slender rod	—	+	—	Pink	+	—	—	—	sl.	—	—	—	—	—
C11	40,000	Large rod	+	—	+	—	sl.	—	—	—	+	—	+	—	—	—
B101	40,000	Medium rod	—	+	—	Brown	+	—	—	—	—	—	—	—	—	—
C5	20,000	Coccus	—	—	+	Yellow	—	—	—	—	—	+	+	—	+	—
C6	20,000	Coccus	—	—	—	Brown	—	—	—	—	—	+	+	—	—	—
C12	20,000	Short rod	—	—	—	—	sl.	—	+	+	—	—	+	—	—	—
A1	20,000	Short rod	—	—	—	—	sl.	—	—	—	—	—	—	—	—	—
B4	20,000	Medium rod	—	—	—	—	—	—	—	—	—	—	—	—	—	—
C106	20,000	Large rod	+	+	—	—	sl.	—	—	—	+	—	+	—	—	—
CX3	20,000	Slender rod	—	+	—	Yellow	sl.	—	—	—	—	—	—	—	—	—

+ positive, — negative, sl. slight, + — acid but no gas, — — no acid or gas.

Over 100 cultures were studied. This number was reduced by cultural and morphological tests to 23 that could be presumed to be distinct species. Of these, 16 appeared on the nutrient agar, 7 on albumin agar, and 6 on soil-extract agar, identical species appearing in some cases on two or on all three media. As the nutrient agar gave not only the highest total count but also exhibited the greatest number of types, the determinations in table 3 refer to this medium. The data refer to low temperature observations, all cultures

being kept at 3°C. for 15 days—though gelatine and milk tubes were kept 4 weeks—before final observations were made.

In classifying the cultures, it was frequently found that certain strains, although macroscopically and microscopically similar, differed in some characteristics from the majority of the type. These differences were generally with respect to nitrate reduction, or to acid or ammonia production, and were not considered sufficiently distinctive for separate classification. The short rod forms, on the other hand, showed in many cases a similar microscopic appearance both as to size and grouping. The types given in the table, however, showed macroscopic as well as biochemical differences which appeared to warrant specific distinction.

The great majority of the bacteria growing at 3°C. on nutrient agar were found to be short rods which appeared usually as punctiform or small lens-shaped colonies. These were non-sporulating bacteria, 0.5 to 1.4 $\mu$  long, 0.3 to 0.5 $\mu$  wide, growing singly or in pairs, chains never having been observed. Another group composed of slender rods, 1 to 2.5 $\mu$  long, 0.3 $\mu$  wide, the colonies of which were brown to yellow in color, was much less numerous than the short rods. The larger rods and micrococci formed even less numerous groups.

A very limited number of types appeared to predominate on the 3° plates, the overwhelming majority of the colonies being representatives of but two types. The most abundant organism (A7), comprising more than half the colonies, appears to correspond to the most abundant type of the non-spore-forming organisms described by Conn (6), namely the non-chromogenic, slowly liquefying type of "slow growers." Although our cultures were all kept at 3°C., the characteristics, as far as determined, appear similar to this type. Our second type in point of abundance, incapable of liquefaction, likewise appears to coincide with the non-chromogenic, non-liquefying type of Conn which appeared as the second most numerous type, the reduction of nitrates being the only apparent point of difference. This feature is to be regarded, however, as somewhat variable.

As all the types described above grew rather better (some much better) at 20° than at 3°, none of the cultures represent truly psychrophilic organisms. It would appear rather that the bacteria of frozen soil, even those capable of low temperature growth, represent types which are common to soil at other seasons rather than a distinct winter microflora.

#### SUMMARY

A study was made of bacterial types in field soil which had been frozen for more than two months.

Determinations were made of the frequency of various types developing on albumin agar plates at 20° and at 3° respectively. Apart from Actinomyces which did not develop at the low temperature, the number of colonies appearing at 3° was less than 10 per cent of those at 20°, most of the bacteria of frozen soil being incapable of low temperature growth.



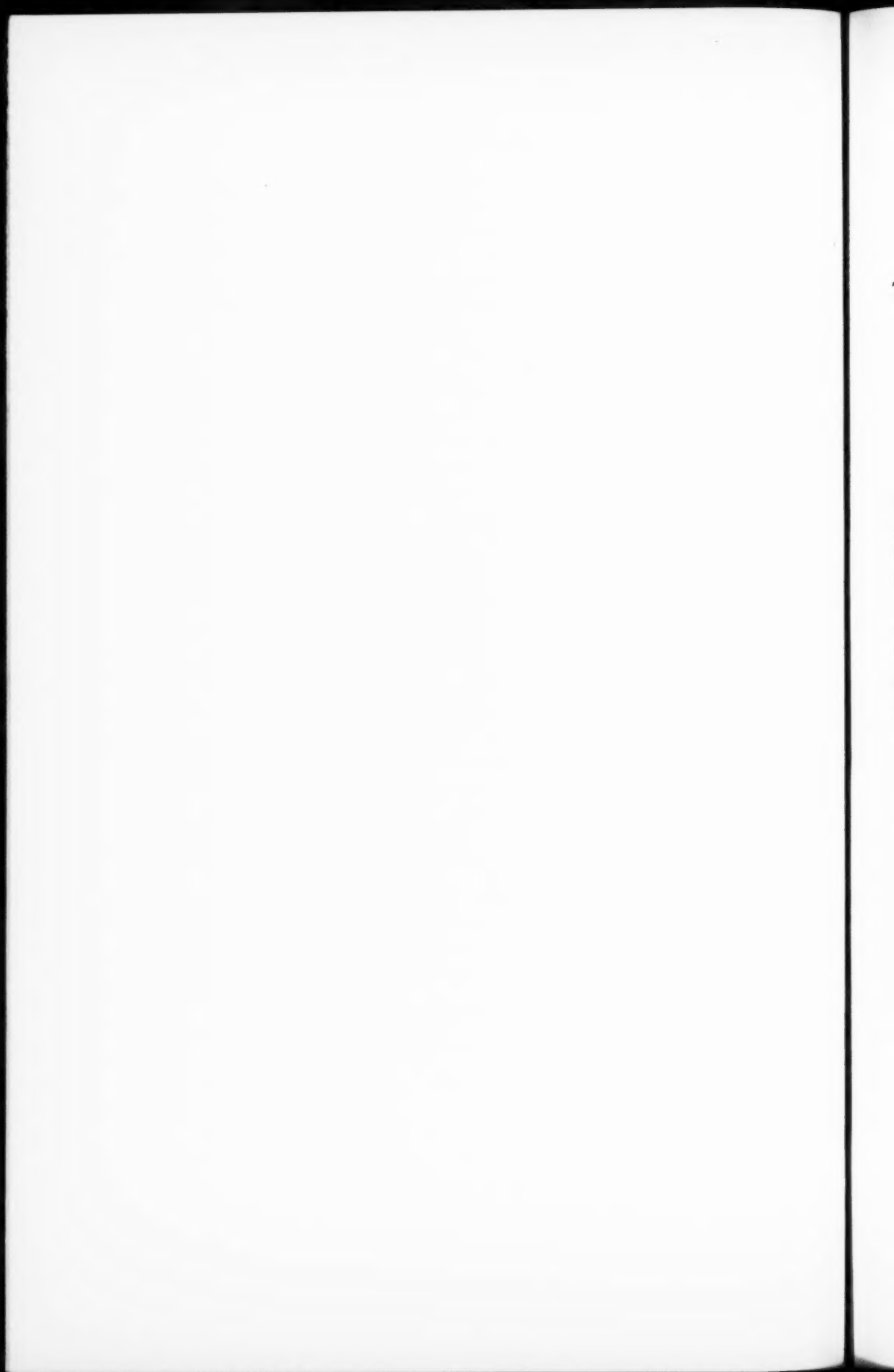
At 20° the most abundant type was the group of non-sporulating short rods, non-liquefying or slowly liquefying, and the next most abundant group was that of Actinomycetes. Rapidly liquefying rods and micrococci were found to be numerically unimportant. At 3° the non-liquefying or slowly liquefying short rods formed a higher proportion of the bacterial colonies, the other groups showing even less capability for low temperature growth than these forms.

The microflora of frozen soils does not appear to exhibit characteristics different from that of other seasons.

Sixteen type species, isolated from nutrient agar plates at 3°C. have been described, as well as their approximate frequency. Two types predominate—both non-sporulating short rods—one slowly liquefying, one non-liquefying, and appear to be representative soil types of other seasons which develop better at more moderate temperatures.

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# THE PRODUCTION AND USE OF SULFATE IN HUMID AND ARID SOILS AS AFFECTED BY CROPPING AND SULFUR TREATMENTS<sup>1</sup>

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The application of elemental sulfur to different types of soils has produced varied and non-uniform results. Crop response from applications of sulfur does not necessarily vary as the total amount of sulfur in the soil. In fact, a determination of the total soluble sulfate at any one time does not seem to be an index of the result that can be expected from sulfur fertilization.

It is generally believed that sulfur needed in the nutrition of the plant is taken up in the sulfate form, and the indirect effects from the use of elemental sulfur in making soluble certain other plant-food elements, such as calcium, potassium, and phosphorus, also depend upon its oxidation in the soil to sulfate. Whatever may be the direct action of sulfur upon the soil, it seems quite certain that the production of a suitable supply of sulfate throughout a considerable part of the growing season, either from the soil supply, or from that added as a fertilizer, is essential for plant growth.

A great many papers on sulfur in its relation to agriculture have been published, and since the data up to 1922 have been well summarized by Joffe (8) it appears unnecessary to include a general review of the literature on the subject in this paper. Most investigations on sulfur oxidation have been with uncropped soils; some have been with soils under crop; but a careful survey of the literature fails to reveal any investigations which have been comparative on cropped and uncropped soils of different reaction and of known response to field applications of sulfur.

In the light of our present knowledge of the relations of soils and crops it appears reasonable to believe that sulfate production and accumulation in a cropped soil might be different from that in the same soil when fallowed, and that the crop might not affect all soils alike.

<sup>1</sup> Part of a thesis submitted to the Graduate School of the University of Missouri, in partial fulfillment of the requirements for the degree of Master of Arts, June, 1925.

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Acknowledgment for many valuable suggestions and criticisms, is due Dr. F. L. Duley of the University of Missouri, under whose direction this study was made.

## OBJECT OF THIS INVESTIGATION

This research was planned to study the effect of the crop on sulfate production in different soils, the effect of such sulfate on soil reaction, on crop growth, and on percentage of sulfur in the crop. As a secondary consideration some data have been secured relative to the recuperative powers of the various soils studied for sulfate after a depletion has taken place as the result of cropping.

## EXPERIMENTAL

*Soils*

The soils used in this study include: a sandy loam from Vale, Oregon, which has not responded to sulfur fertilizers; a medium sand from Redmond, Oregon, which has produced from  $\frac{1}{3}$  to  $\frac{1}{2}$  more alfalfa as a result of sulfur treatments; Eldon Silt Loam from Missouri, which has given some response to sulfur treatments; and Putnam Silt Loam from Northern Missouri, which has shown no

TABLE 1  
*Determination of total sulfur, of sulfate sulfur, and of acidity in the different soils at beginning of the experiment*

SOILS	TOTAL AMOUNT OF SULFUR PER 2,000,000 POUNDS SOIL	SULFATE SULFUR	pH	LIME RE- QUIREMENT, TRUOG METHOD
	<i>pounds</i>	<i>p.p.m.</i>		
Vale sandy loam.....	1096	47	7.4	None
Redmond medium sand.....	646	21	7.0	None
Eldon silt loam.....	440	6	6.0	Medium
Putnam silt loam.....	1130	10	5.7	Strong

indication of needing sulfur fertilizer treatments. The sulfur conditons of these soils are summarized in table 1. It will be noticed that the Vale and Putnam soils are both high in total sulfur but that they are extremely different in pH and are representative, one of the semi-arid and the other of the humid section. The Redmond soil and Eldon soil are both low in total sulfur, have a smaller range in pH, and represent soils one from the semi-arid and the other from a humid section, both of which have responded to sulfur treatments.

*Methods*

Weighed amounts of each of these soils were placed in gallon jars and five applications of each of the following were made to each soil: check, sulfur 150 pounds per acre, sulfur 500 pounds per acre; triplicate treatments with  $\text{CaCO}_3$  plus 150 pounds of sulfur per acre were made to additional jars of the Eldon and Putnam soils.

The treatments having been mixed thoroughly with the soil which was then compacted to approach field conditions, the jars were placed in the green-

house. One series, including a jar of each treatment and soil, was kept fallow and the remainder were seeded to soybeans. All jars were kept at approximately optimum moisture with distilled water throughout the period of study. At the end of 38 days one series was harvested, the roots were carefully removed and soil samples taken for sulfate and pH determination. The total crop was dried, the yield secured, and determinations were made of the total sulfur content.

The fallowed jars were sampled at the same time, a soil auger was used and the hole was filled later with surface soil. The location of the borings were recorded in order to avoid sampling in the same place at a later date.

At the time of taking down the first series of jars it became apparent that the soybean crop would neither give the growth desired nor continue growing long enough for the purposes of the experiment, therefore, alfalfa was seeded with the soybeans on the remaining cropped jars. At the end of 77 days from the beginning of the experiment, a second set of jars was taken down, and at the end of 120 days a third set was harvested and sampled. The same procedure in sampling, crop removal, and analysis was followed as at the end of the first period.

Hydrogen-ion determinations were made from 1-2 water extracts; the colorimetric method of Gillespie (3) being employed. Sulfate determinations were made from 1-5 water extracts, 10 per cent aluminum chloride being used as a flocculant. The sulfate sulfur was then determined by the turbidity method of Schreiner and Failyer (9). A "Campbell-Hurley" colorimeter was used and uniform light conditions were insured by making the comparisons at night and reflecting light with a desk lamp from white blotting paper located a uniform distance from the reflector. Total sulfur in the crop was determined by a modification of the method proposed by Wolcott (14) for soils. Total sulfur in soils was determined by fusion with sodium carbonate, a modification of the Hillebrand (5) method being employed.

#### RESULTS

A uniform stand of soybeans and alfalfa was secured and although considerable difference was noted in the crop growth when different soils were compared, there was little consistent variation in any soil as a result of sulfur treatments. This was true even with the Redmond soil which has responded to field applications of this element. Such a condition was not unexpected, since crop growth secured under the limited time of this experiment was not enough to deplete the soil of the natural stored supply of sulfate.

#### *Effect of Sulfur Applications to Soil on Sulfur Content of Crops*

The pH and the sulfur present in the crop for the various periods are recorded in table 2, and the sulfate sulfur in soil and crop for the same periods, in table 3. It will be noticed that for any one soil the percentage of sulfur in crops

increases almost directly with the sulfur applications and the consequent increase in sulfate. When different soils are compared, however, the sulfur content in the crops does not increase with an increase in the soluble sulfur content of the soil. In some cases, however, because of the larger yield secured, the total weight of sulfur absorbed by each jar increases with a larger sulfate content in the soil.

The results secured at the end of the first period are of most value in studying this condition because of the fact that all jars had a uniform stand of soybeans with no alfalfa. In figure 1 the sulfate sulfur, pH and percentage of sulfur in the crop on soils treated with 150 pounds of sulfur per acre, are compared

TABLE 2  
*Effect of H-ion concentration of soil on the percentage of sulfur in crop*

SOIL*	AFTER 38 DAYS		AFTER 77 DAYS		AFTER 120 DAYS	
	pH	Sulfur in crop	pH	Sulfur in crop	pH	Sulfur in crop
		<i>per cent</i>		<i>per cent</i>		<i>per cent</i>
Vale—X.....	7.3	0.262	7.4	0.250	7.5	0.283
Sulfur 150.....	7.2	0.302	7.2	0.336	7.3	0.317
Sulfur 500.....	7.0	0.324	7.0	0.348	7.0	0.363
Redmond—X.....	6.9	0.278	7.0	0.200	7.0	0.241
Sulfur 150.....	6.7	0.304	6.8	0.232	6.8	0.333
Sulfur 500.....	6.5	0.388	6.5	0.438	6.6	0.441
Eldon—X.....	5.5	0.280	5.8	0.298	5.9	0.265
Sulfur 150.....	5.3	0.316	5.5	0.340	5.7	0.509
Sulfur 500.....	4.9	0.340	5.3	0.516	5.4	0.895
CaCO <sub>3</sub> 3000.....	6.8	0.302			6.8	0.399
CaCO <sub>3</sub> 3000 } Sulfur 150 }	6.6	0.346			6.7	0.398
Putnam—X.....	5.6	0.316	5.7	0.258	5.7	0.296
Sulfur 150.....	5.3	0.326	5.4	0.408	5.5	0.381
Sulfur 500.....	4.8	0.420	4.9	0.580	5.3	0.762

\* Treatments are recorded as pounds per acre.

for the various soils. It will be seen when any treatment for the various soils is compared, that the percentage of sulfur in the crop has no tendency to increase with an increase in the soluble sulfate in the soil, but is very closely correlated with increased acidity. With the exception of the Putnam silt loam there is a decided increase in the percentage sulfur in the crop with a decrease in pH value. The crops from the Putnam jars have a higher sulfur content than any of the others, but the pH averages about the same as similarly treated jars of the Eldon soil. The pH is, however, decidedly lower than either of the two western soils as is the percentage of sulfate in the soil.

On the other hand the percentage of sulfur in the crop is distinctly higher in the more acid soil, in spite of its lower sulfate content. Calcium carbonate added to jars of the Eldon soil raised the pH to that of part of the Redmond jars. The percentage of sulfur in crops grown on jars of these two soils with corresponding pH values was practically the same, regardless of the treatment.

With one exception, the sulfate content in the Vale soil is higher with all treatments than any of the other soils receiving similar treatment and yet the

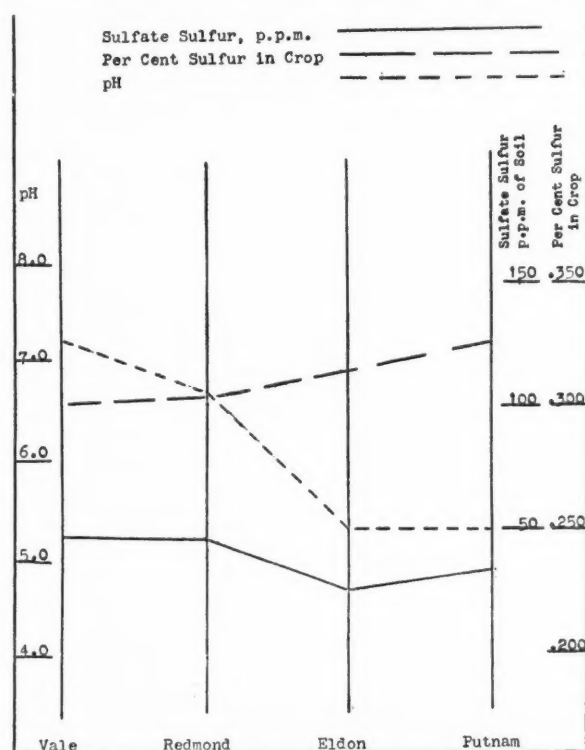


FIG. 1. COMPARISON OF SULFATE SULFUR, pH AND PERCENTAGE OF SULFUR IN THE CROP ON SOILS TREATED WITH 150 POUNDS OF SULFUR PER ACRE

sulfur content of the crops grown on the soil was lower than in the crops grown on the other soils. Although these data are not complete enough to be conclusive, they are of interest in showing additional differences in the effect of sulfate on various soils. It would appear, for instance, that soybeans can secure sulfate more readily from the limited supply in the unlimited jars of the Eldon soil than from the more abundant supply of the western soils, and this might help to explain why this soil, though very low in total sulfur and appar-



ently in sulfute sulfur, gives only a slight response to sulfur treatments when compared to the Redmond soil.

Robbins (11) has found anions to be absorbed more readily from a medium with a reaction on the acid side of the isoelectric point for plant protein. The present work offers some confirmation of this for the sulfate ion. These results are also in accord with the work of Hoagland (6) who has found a greater

TABLE 3  
*Sulfate sulfur produced in cropped and in fallowed soils*

SOIL TREATMENT*	AFTER 38 DAYS		AFTER 77 DAYS		AFTER 120 DAYS	
	Cropped†	Fallow	Cropped†	Fallow	Cropped†	Fallow
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
<b>Vale:</b>						
Check.....	52.0	20.0	72.0	80.0	91.3	85.0
Sulfur 150.....	49.5	28.3	91.2	95.3	100.7	189.0
Sulfur 500.....	112.8	67.8	130.3	216.7	225.4	270.0
<b>Redmond:</b>						
Check.....	26.1	17.1	33.6	41.0	26.2	33.0
Sulfur 150.....	47.5	53.3	68.2	107.0	82.5	239.0
Sulfur 500.....	48.8	76.0	80.2	116.0	202.0	266.0
<b>Eldon:</b>						
Check.....	8.8	4.7	11.0	6.7	13.1	7.3
Sulfur 150.....	27.6	16.0	52.8	60.6	46.6	59.0
Sulfur 500.....	74.1	60.0	86.8	180.0	117.9	175.0
CaCO <sub>3</sub> 3000.....	13.5	5.7	....	....	33.0	13.0
Sulfur 150 }.....	34.8	30.3	....	....	89.5	64.0
CaCO <sub>3</sub> 3000 }						
<b>Putnam:</b>						
Check.....	10.7	6.0	9.3	8.6	28.2	10.0
Sulfur 150.....	34.4	17.3	78.7	60.7	87.7	71.0
Sulfur 500.....	91.2	45.7	110.4	117.0	150.9	150.0
CaCO <sub>3</sub> 5500.....	23.5	9.3	....	....	....	29.0
CaCO <sub>3</sub> 5500 }.....	42.1	24.0	....	....	....	135.0
Sulfur 150 }						

\* Treatments are recorded in pounds per acre.

† The figures in the "Cropped" column represent the sulfur in the crop calculated to p.p.m. of soil, plus the sulfate sulfur in the soil at the time of harvest.

absorption of anions in an acid media, and of Joffe (7) who has found that lowering the pH by the addition of sulfuric acid to soils results in a higher percentage of nitrogen in the alfalfa produced.

#### SULFATE PRODUCTION IN CROPPED AND FALLOWED SOILS

The figures representing the sulfate production on the cropped soil were secured by determining the total sulfur in the crop produced, calculating this

to parts per million of soil and adding it to the sulfate sulfur found in the soil at the time of harvest. This procedure is based on the general assumption that crops take up all their sulfur in the sulfate form, and also on the particular assumption that practically all the roots and crops were secured. Special care was taken in removing the roots and although a portion of the very fine ones were not secured, the loss in this respect is thought to be very small.

The sulfate sulfur produced in cropped and in un-cropped soils is reported in table 3. It will be noticed that there is a general increase in sulfate on all soils

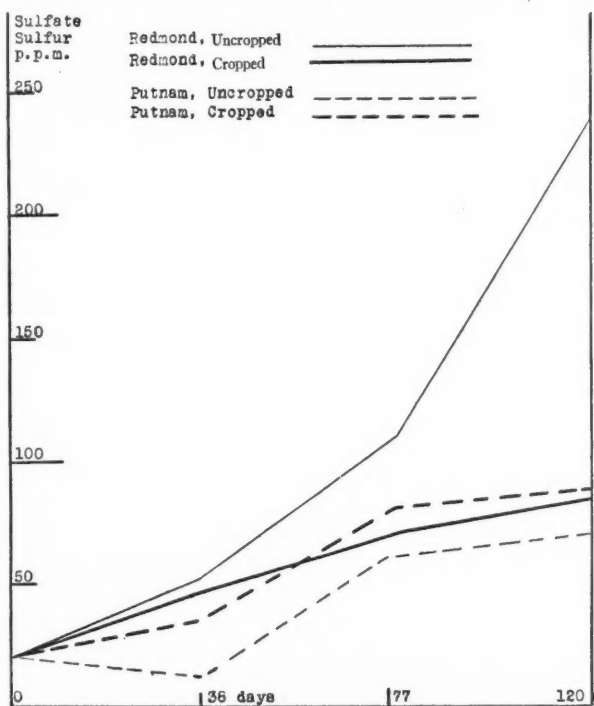


FIG. 2. SULFATE PRODUCED ON CROPPED AND UNCROPPED PUTNAM AND REDMOND SOILS TREATED WITH 150 POUNDS OF SULFUR PER ACRE

as a result of sulfur applications and that the sulfate accumulation is greater at the end of the longer period. The sulfate content of the untreated jars changed but little during the course of the experiment in the case of the two Missouri soils, especially in the fallowed jars. Considerable increase with time is apparent in the case of the Vale soil, and to a lesser extent, in the Redmond soil. The effect of the 150 and 500-pound sulfur treatments has been to increase the sulfate for both cropped and fallowed soils at the various stages sampled. Sulfate production in the case of the two acid soils approaches a

maximum at the end of the second period, while an increase throughout the period of study is apparent in the case of the two western soils.

#### *Effect of Crops on Sulfate Production*

With all treatments on Putnam silt loam and on untreated jars of the Eldon soil, sulfate production was stimulated by cropping, whereas with all other soils and treatments the reverse was true. The most striking difference is between the Putnam and Redmond soils, the former an acid soil from the humid section which does not require sulfur fertilization and the latter a neutral soil from the semi-arid section on which field applications of sulfur have given marked increases in yield.

Uniform differences in the sulfate produced are found with the 150-pound sulfur treatment (Fig. 2). The difference in favor of the cropped jars is uniform for all three periods in the case of the Putnam soil, whereas with the Redmond soil the curve representing the fallowed jars is higher than that of the cropped soil, the difference becoming constantly greater toward the end of the last period.

In all the soils but the Redmond the crop tended to increase the amount of sulfate produced during the early stages of growth; namely, until the end of the first period. After this time the fallowed soils were more efficient in sulfonation, except as has been noted with the Putnam soil and with the untreated jars of the Eldon silt loam.

It is interesting to compare these results with those secured by other investigators with the effect of crop growth on nitrate production. Lyon, Bizzell and Wilson (9) found that maize did not depress nitrate accumulation during the early growth, but did so later. Wheat, unlike maize, showed a depressing influence at the end of the first period and continued to exert this depression throughout the entire period of growth. These authors explain this phenomenon as being due to the liberation by the plant roots of non-nitrogenous organic matter which is thought to favor the development of nitrate-consuming organisms in the soil with the consequent transformation of nitrate into other nitrogenous substances. Lyon and his colleagues worked with a heavy silty clay loam soil and believe that with a more highly aerated soil the depression of nitrate accumulation might not occur, since the organic acids liberated would be more completely oxidized. Texture has not had this effect in the present study. The depressing effect of the crop on sulfate formation has been most pronounced on a loose sandy loam soil, whereas on the heaviest and least aerated of the soils studied the crop stimulated sulfate production.

Greaves (4) quotes McBeth and Smith to the effect that plots continuously cropped to alfalfa, potatoes, oats, and corn, all show a higher nitrifying power than do corresponding fallow plots, with the greatest stimulation occurring from alfalfa. It would appear that probably the stimulating or depressing

effect of the crop on nitrification may vary with different soils, as has been shown for sulfonation in the present study.

#### THE RECUPERATIVE POWER OF SOILS FOR SULFATE

##### *After depletion by crop*

Some work was done to test the power of the soils studied to build up in total sulfate after the supply has been depleted. After removing the roots and sampling the soils from the cropped jars at the end of the second period, the soil was returned to the jars and was kept up in moisture content for 12 weeks.

TABLE 4  
*Recuperative power soils for sulfate (after depletion by cropping)*

SOIL AND TREATMENT*	SULFATE SULFUR AT TIME OF HARVEST	SULFATE SULFUR LOSS OR GAIN	
		7 weeks after harvest	12 weeks after harvest
	p.p.m.	p.p.m.	p.p.m.
Vale:			
Check.....	64.0	+28.0	+26.0
Sulfur 150.....	79.0	+28.0	+29.0
Sulfur 500.....	119.0	+11.0	+119.0
Redmond:			
Check.....	25.0	-6.0	-3.0
Sulfur 150.....	60.0	-28.0	-13.0
Sulfur 500.....	61.0	+5.2	+77.0
Eldon:			
Check.....	3.7	-0.7	+5.3
Sulfur 150.....	45.0	-8.0	-9.0
Sulfur 500.....	72.0	+2.0	+48.0
Putnam:			
Check.....	2.3	+1.7	+13.7
Sulfur 150.....	68.0	-28.0	-23.0
Sulfur 500.....	96.0	+20.0	+48.0

\* Treatments are recorded in pounds per acre.

At the end of 7 weeks and again after 12 weeks from the date of harvest, samples were taken and the water-soluble sulfate was determined. The results are recorded in table 4. It will be noted that although the data secured are not uniform and probably do not represent enough trials to warrant definite assumptions, some rather interesting conditions are indicated.

The general difference, between the soils that have shown a need for sulfur and those which do not profit from its use is very well defined, particularly in case of the untreated soils. The Vale soil has built up quickly in sulfate after the crop was removed and this was true to a lesser extent with Putnam silt

loam. In the Redmond and the Eldon silt loam, however, the supply of sulfate is increased very slowly after a depletion by cropping. This difference in the recuperative power for sulfate accumulation may explain in part the variation in response to sulfur fertilizers, especially where permanent crops such as alfalfa are produced.

#### *Percolation tests*

In order to test this point further, percolation tubes containing 1500 and 1600 gm. of the Putnam and Redmond soils, respectively, were set up and leached with distilled water until the percolate failed to give a qualitative test for sulfate. Aliquots of the percolate were taken, and the sulfate was determined and calculated as parts per million of sulfate sulfur on the basis of the water-free weight of the soil. The tubes were kept in the laboratory and maintained at optimum moisture with distilled water for a period of 14 weeks after which they were again leached and the percolate analyzed in the same

TABLE 5  
*Recuperative power of soils for sulfate (percolation trials)*

SOIL	SULFATE SULFUR IN PERCOLATE	
	At start	After 14 weeks
	<i>p.p.m.</i>	<i>p.p.m.</i>
Redmond medium sand.....	45.31	15.87
Duplicate.....	43.06	15.62
Average.....	44.18	15.74
Putnam silt loam.....	32.68	26.70
Duplicate.....	34.02	29.15
Average.....	33.35	27.92

way. The results of duplicate percolation tubes from each of the two soils are recorded in table 5.

It will be noted that the Redmond soil, which had the highest sulfate content at the time of the first leaching, built up its sulfate supply only 15.7 p.p.m. at the end of 14 weeks, whereas the Putnam soil, which had a lower total sulfate content in the first percolate, increased to approximately 28 p.p.m. These figures are in accord with the results secured by comparing the increase after cropping. The difference in favor of the Putnam soil was really greater than is apparent in this table, as it was impossible, because of the way the soil had run together by the end of the second period, to leach out all the sulfate.

#### DISCUSSION

Of the soils studied, Redmond medium sand not only needs a higher percentage of sulfate for proper crop growth, but its ability to produce sulfate has been reduced by cropping, and the power of this soil to build up in sulfate,

after a depletion by cropping, appears to be insufficient to supply the needs of the crop. The Vale soil also required a high sulfate content for the use of crops, but the sulfofying capacity was so great and the total sulfur content so high that an abundant supply of sulfate was maintained. The Eldon soil apparently did not require a large amount of sulfate for crop production. Its need for sulfur treatments seemed to be due largely to the low percentage of total sulfur and to the fact that it did not build up in sulfate quickly after a depletion by cropping. The Putnam soil not only made an efficient use of its sulfate but the rate of sulfification was increased so markedly by cropping that the small amount of sulfate required was maintained throughout the growth period. This soil also quickly built up a supply of sulfate after the crop was removed.

The points which have just been discussed are not brought out in a study of the uncropped soil. It would appear that these differences in the sulfur relations of soils and crops are of importance in explaining the fact that a need for sulfur fertilization has not been apparent on many middle western soils with as low a total sulfur and sulfate content as some semi-arid soils on which yields have been greatly increased by field applications of sulfur fertilizer.

#### CONCLUSIONS

Under the conditions of these tests, the crop grown on the western soil that has given returns for sulfur, has retarded the formation of sulfate. Crop growth on the humid soils has increased the production of sulfate and thus probably has helped to supply the crop with this material.

Under conditions of higher H-ion concentration as was the case with the humid soils it seems probable that crops may be able to extract sulfur more readily from the soil and therefore not require so great a continuous supply as when grown on semi-arid soils. Furthermore, humid soils may recuperate more readily in their sulfate content, and hence have a sufficient supply of sulfate for the crop at practically all times. On the other hand, it would be more difficult for some of the semi-arid soils, such as the one from Redmond used in this work, to regain enough sulfate for satisfactory growth, after it once had been depleted. This condition most likely would be found in field practice where perennial sod crops have occupied the land for considerable time, and may offer some explanation for the marked returns that have been obtained from the use of sulfur on certain alfalfa lands in the semi-arid regions of the West.

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